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QUALITATIVE ANALYSIS**

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FRONTSPICE.—Students using semi-micro methods. (*Picture taken at Oklahoma Agricultural and Mechanical College.*)

SEMI-MICRO QUALITATIVE ANALYSIS

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PREFACE

One of the recent advances made in analytical chemistry, from the standpoints of both education and practice, is the development of the semi-micro technique. Although its spread was greatly retarded by scarcity of textbooks using semi-micro methods, its marked advantages—lower expense to the student, increased accuracy, greater skill and respect for cleanliness, and the ability to cover more and varied work in the allotted time—have led many progressive educators to adopt it.

The purpose of this book is to present a system of semi-micro qualitative analysis in such manner as to make it clear, easily understood, and, as far as possible, self-administering. No teacher need hesitate to adopt the method, for any student or instructor can readily acquire the skills necessary in the handling of small amounts and the identification of the product of the reactions.

The scheme used is little different from the customary macro procedure, only the technique and a few of the reagents being changed. Little actual dependence is placed on organic reagents, as the authors feel that inorganic reactions, which are more easily understood by the student, should be emphasized. Some use of the better organic reagents is made, however, to acquaint the student with the advantages and disadvantages of the most dependable ones. Thus, while the characteristic reactions of the ions and the laws of chemistry receive chief emphasis, the practical aspects are not overlooked.

Since qualitative analysis in most schools is taught as part of general chemistry in the second semester or the third quarter of the freshman year, this text purposely

has been kept small and the treatment of the theoretical portion very simple and brief. The discussion in the earlier part is chiefly qualitative, and develops the theory in terms of the older, standard conceptions. This is followed by a section dealing with some of the more modern theories, presented in such manner as to make it easy for the student to apply the newer conceptions to the theories studied previously. Care has been used to keep that balance between theory and technique which is desired for the average student in qualitative analysis. Extensive use has been made of supplementary notes to maintain a close connection between laboratory and theory.

The derivations of various formulas have been largely omitted in view of the fact that in many schools the instructors prefer to leave such derivations to be considered in physical chemistry. In such cases, inclusion of these derivations serves only to confuse the students.

It has been the experience of the authors that students often get different types of problems confused when they are considered separately. For this reason, the methods of working problems are considered collectively in a section following the discussion of the theory. This policy has the advantage of enabling the students to compare the various types of problems and the added advantage of enforcing a review of the theories underlying the problems, at a time when it is most profitable to the student.

The present book evolved from the experiences and criticisms of both teachers and students during its use in manuscript form for seven semesters at Oklahoma Agricultural and Mechanical College, where it has been used in the instruction of students of the freshman and sophomore levels. In spite of its small size, the book contains sufficient information, technique, and instructions to permit combining it with any standard reference book for a longer course when desired. Sufficient source material and references have been included to maintain the interest

of the more zealous students. A careful study of the references listed would give any investigator an excellent background for research in this field.

The authors wish to acknowledge the debt they owe to Dr. Paul Spoerri, who, through his course at Polytechnic Institute of Brooklyn, demonstrated that semi-micro technique could be used successfully with the ordinary analytical scheme by freshmen and sophomore students and whose notes were the source of many valuable ideas. Also grateful acknowledgment is accorded Dr. O. C. Dermer, Dr. H. M. Trimble, and other colleagues for helpful material, criticisms, and suggestions.

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O. M. SMITH.

STILLWATER, OKLAHOMA,
January, 1938.

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SEMI-MICRO QUALITATIVE ANALYSIS

INTRODUCTION

Too often it happens that a student enters a new course having only a vague idea of what the course is about and for what he will be held responsible. This is especially true of the usual course in qualitative analysis. Qualitative analysis is far more than a course in analytical procedure, and, for the student to get the most value from the course, it is important that he understand, from the first, what he is expected to learn. The most important of the things that should be gained during the course are:

1. Experience in the handling of certain types of apparatus rapidly and efficiently.

2. Experience in making observations and drawing correct conclusions from them.

3. A greater knowledge of the chemistry of metals, cations and anions, and of the laws and principles of chemistry.

4. An appreciation of the great necessity for cleanliness of apparatus and purity of reagents in all chemical reactions.

5. A knowledge of the methods used in carrying out practical analyses of samples whose chemical composition is not known.

It will be noticed that the practical knowledge of analytical methods is perhaps the least important to most chemists since an analysis can be made such routine procedure that little knowledge of chemistry is required for its use. If some unusual problem comes up, however, a

knowledge of the laws and of the chemical characteristics of different ions becomes exceedingly important. In this connection, it will be found that a review of inorganic chemistry will enable the student to work more efficiently and will eliminate to a large extent the unfamiliarity which accompanies entrance into a new course. Special emphasis should be placed on the laws of ionization and ionic reactions and on the chemical properties of the metals.

The complete analysis of a substance consists in the determination of the chemical composition of that substance. The first step in any analysis is to determine the *nature* of the elements or ions present. This process is known as *qualitative* analysis. *Quantitative* analysis consists of determining the weights of the constituent present in a given sample of the substance.

PART I

SEMI-MICRO METHODS

SEMI-MICRO TECHNIQUE

During the last few years much effort has been expended in attempts to develop apparatus and special technique for the analysis of very small quantities of material. Dealing with samples of only 3 to 5 mg. (compared with the usual 0.5 to 1.0 g. macro sample), the micro method consumes much less time for reactions to become complete, requires much smaller quantities of reagents, requires much less of the sometimes rare and valuable unknown, occupies much less laboratory space, and in many other ways proves superior to the macro methods.

Unfortunately, before a student can successfully undertake the study of the real micro analysis, he must be experienced in the handling of delicate precise instruments and must have a fair knowledge of chemistry. For this reason, a technique which approaches micro methods and incorporates many of their advantages, yet remains sufficiently simple to be used by students in the second year of chemistry, has been devised. This procedure, known as *semi-micro* qualitative analysis, makes use of the simpler micro methods but works with samples about one-twenty-fifth as large as the macro samples (or about forty times as large as a micro sample).

The unknown may be encountered in solution or as a solid. An analysis consists chiefly of a series of precipitations and re-solutions. Hence, it is necessary that the unknown be placed in solution (unless already dissolved) before the analysis can start. These steps require the

careful use of special methods, and it is essential that skill in these techniques be developed early in the course. Many analyses fail because the student is awkward in carrying out separations of solids and liquids or because evaporations are carried too far. Each of the more important procedures will be discussed under its own heading.

Filtrations. In semi-microanalysis the usual filter paper and funnel are not used. Instead, the mixture of liquid

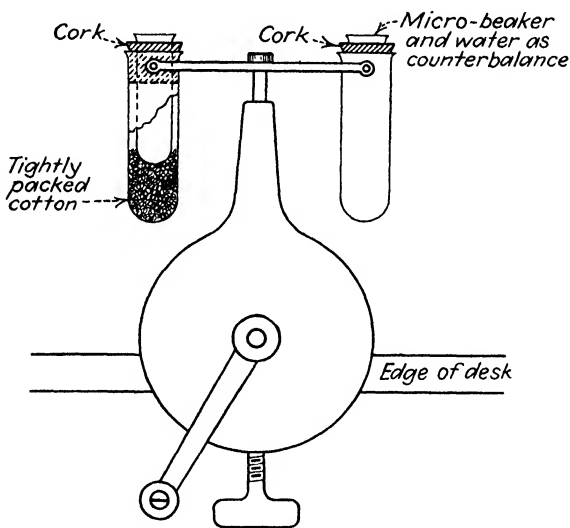


FIG. 1 -Centrifuge.

and solid is placed in a cone-shaped centrifuge tube or a microbeaker, and the tube is placed in one of the cups of a centrifuge (Fig. 1). Another tube the same size as the first, containing a volume of water equal to the volume of material in the first tube, is placed in the centrifuge exactly across the head from the first tube. Thus balanced, the centrifuge will have a minimum of vibration. If a hand centrifuge is used, it must be turned with sufficient velocity that the centrifugal force will pack the precipitate in the

tip of the cone-shaped tube leaving the liquid above the precipitate clear. The centrifuge should always be allowed to slow down to a stop of its own accord. Any attempt to quickly stop the instrument may result in damage to the centrifuge. The electrically driven centrifuges are so constructed as to provide for the necessary velocity, automatically. Several types of electrically driven centrifuges are on the market, many of which have variable speed control and should be operated according to instructions accompanying the instrument.

The filtrate may be removed by means of an ordinary medicine dropper. Into the tip of the dropper is inserted a tight twist of absorbent cotton which is cut off $\frac{1}{8}$ in. below the glass tip with scissors. This serves as a filter. The bulb of the dropper is compressed, the tip inserted into the liquid, and the bulb slowly released so as to draw the liquid into the dropper tube. The dropper is then withdrawn, the cotton plug removed, and the liquid transferred to a clean micro beaker (Fig. 2).

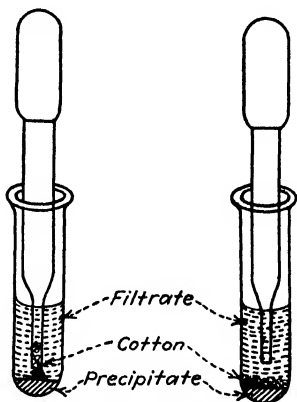


FIG. 2 —Separating filtrate and precipitate after centrifuging.

Occasionally the filtration may be conducted in another manner. The solution is given a preliminary centrifuging after which a very loose cotton plug is placed in the centrifuge tube and pushed just below the surface of the liquid. The tube is replaced in the centrifuge and the latter turned as described earlier. When the tube is removed, the cotton will be found packed firmly over the surface of the precipitate and the medicine dropper can be used without danger of drawing up any of the precipitate.

Handling of Precipitates. It is often necessary to transfer a precipitate from one container to another. For this

purpose a small glass spatula (made as described later) is most suitable. If a liquid reagent is to be added, it can often be used to wash the precipitate from one container to

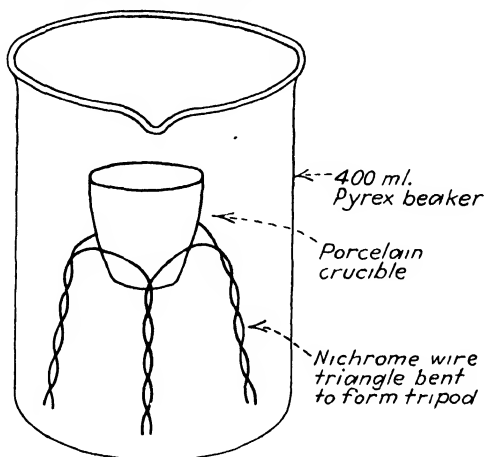


FIG. 3.--Air bath

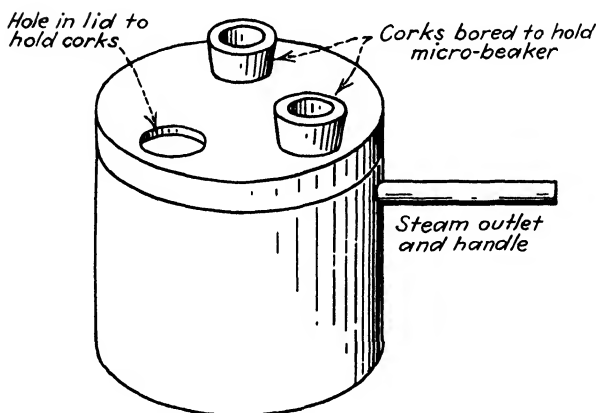


FIG. 4. --Steam bath made from cut-down tin can.

another by agitating the mixture and withdrawing it with a medicine dropper.

Evaporations. Evaporations are usually carried out by placing the liquid in a *crucible* or a *hard-glass* microbeaker

and heating it in an air bath (Fig. 3). *No soft-glass apparatus should ever be used for this purpose unless the evaporation is to be carried out on the steam bath* (Fig. 4) as soft glass will often crack and spill the liquid.

To remove hot containers from the baths, forceps or small tongs are convenient. However, since these implements are generally made of metal which may be corroded, they may contaminate the unknown unless care is used.

Tests for Gases. In testing for ammonium, arsenic, etc., the identification depends on converting the ion into a volatile compound and passing the gas over a bit of filter paper impregnated with the proper reagent to produce a color change. In doing this, the specified amount of the solution to be tested is placed in the gas evolution apparatus (see description of this apparatus, and Fig. 8) and the necessary reagent added. The stopper is inserted, and a bit of filter paper impregnated with the proper reagent is placed in the attached tube. The mouth of the tube is closed with a loose plug of cotton to prevent the entrance of air, and the test tube is warmed. The results can be seen through the side of the glass tube.

Spot Tests. In many cases the identification of a metallic ion will depend on the formation of a precipitate when a drop of the unknown solution is tested by a drop of each of the necessary reagents. Sometimes the resulting precipitate is difficult to see on account of the low concentration of the metallic ion. These tests are best carried out on a watch glass, spot plate, or microscope slide. The proper background is of great importance in rendering a faint precipitate visible. If the precipitate is light in color (white or yellow), a black background (such as a microscope slide painted black on the reverse side, or a piece of black glass) should be used. If the precipitate is dark (red, black, gray, etc.), a white background should be used. A spot plate is excellent for this type of precipitate.

CONSTRUCTION OF APPARATUS

All equipment needed in semi-micro work can be purchased ready for use from any of the larger chemical apparatus supply houses. As yet, however, the small demand has kept prices at higher levels than usual. Consequently, instructions are given here for the conversion of standard equipment into microapparatus. The smaller sizes of macroapparatus may often be used unchanged, and

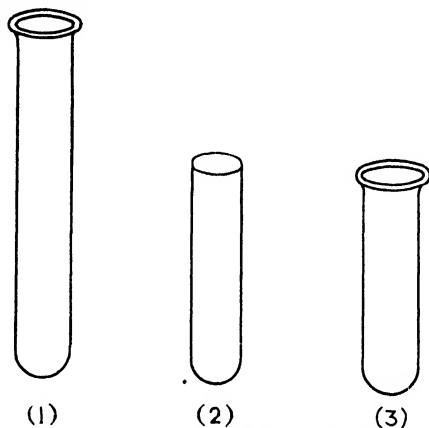


FIG. 5.—Steps in making microbeakers.

most of the other things needed can be constructed by the student from standard equipment. Little knowledge of glass blowing is needed as the student can acquire the necessary skill with very little practice.

Microbeakers. In place of commercial microbeakers, light wall Pyrex test tubes, 75 by 10 mm. diameter, are recommended. Those desiring to use microbeakers of greater diameter may construct them from test tubes as follows (Fig. 5): With a sharp file, make a scratch completely around a 4 by $\frac{1}{2}$ in. test tube about $2\frac{1}{2}$ in. from the bottom. Heat the mouth of the test tube in the flame till it is rather hot then touch it with a drop of water. This will crack the top of the test tube. With a fine wire gauze,

stroke the broken end of the test tube at a 30° angle, and thus polish the tube down to the scratched line (a hot wire glass cutter is more convenient if it is available). Heat the top of the little beaker thus formed, slowly rotating it in the flame until it is relatively soft, and flare the top of the beaker into a rim with the tip of a file or a stick of graphite. About $1\frac{1}{2}$ doz. microbeakers are desirable.

Centrifuge Tubes. These are small containers with cone-shaped bottoms. They may be purchased ready-made or

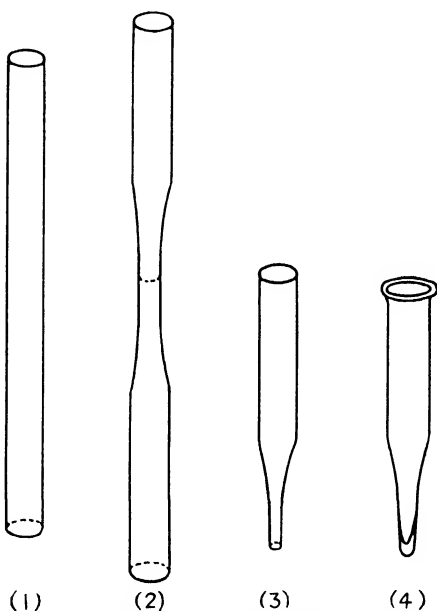


FIG. 6.—Steps in making centrifuge tubes.

may be made as follows (Fig. 6): With a file cut off a 12.5-cm. piece of 12-mm. soft-glass tubing. In the flame of a good Bunsen or high temperature burner, heat a section 2.5 cm. in length exactly in the center of the tube, rotating the tube slowly in the flame to insure uniform heating. When the tube is extremely soft, remove it from the flame and quickly—but steadily—pull the ends of the tube straight out until

the softened portion is only half its original diameter. Allow it to cool to rigidity, then exactly in the center of the constricted portion heat again, rotating as before, pulling the ends of the tube a little at first to narrow the constriction, and finally pulling the tube in two. Seal the two tips thus formed by holding each in a flame until the glass melts into a small drop. If this is done carefully, the *inside* of the tube will be rounded at the bottom. Pointed bottoms should be avoided as they are very difficult to clean. The sharp edges of the top should be fire-polished and flared as was done in making the microbeakers. About $\frac{1}{2}$ doz. tubes will be needed.

Hydrogen Sulfide Generator. To minimize delays and reduce the quantity of hydrogen sulfide escaping into the air, it is advisable that each student prepare his own generator and keep it in his desk. This is easily constructed from a widemouthed 8-oz. bottle which is about 5 or $5\frac{1}{2}$ in. high, a No. 9 or 10 rubber stopper, a 6 by $\frac{3}{4}$ in. test tube, a one-hole No. 2 stopper, and some glass tubing. To one side of the center of the rubber stopper, drill a hole into which a 6 by $\frac{3}{4}$ in. test tube will fit closely, and on the other side drill a small hole about 2 mm. in diameter to act as an air vent. Now heat the extreme bottom of the test tube in a flame till soft, and, from the inside with a long file, push the bottom out into a bulge. Heat the bulge until it is very soft, and, removing it from the flame, quickly blow into the mouth of the test tube until the bulge forms a large bubble. Knock this off with a file. There should then be a hole in the bottom of the tube about 3 mm. in diameter. It should be neither smaller nor much larger. If larger, heat the bottom of the tube once more and press the edges of the hole inward with a file. Let the test tube cool; then *wet* it with water, and push it through the stopper so that, when the stopper is placed in the bottle, the end of the tube will be about 2 mm. above the bottom of the bottle. Next, fit the top of the test tube with the one-hole stopper

and a small right-angle glass tube. Now cut a piece of thick-walled 3-mm. glass tubing 15 cm. long, seal one end in a flame, and blow a bulb (about 7 mm. in diameter) in the center. Cool, then cut the tube off about 1.5 cm. on each side of the bulb. By means of a 1.5-cm. piece of rubber tubing, attach this bulb to the glass right-angled tube. Fill the bulb with a loose plug of cotton; then attach a

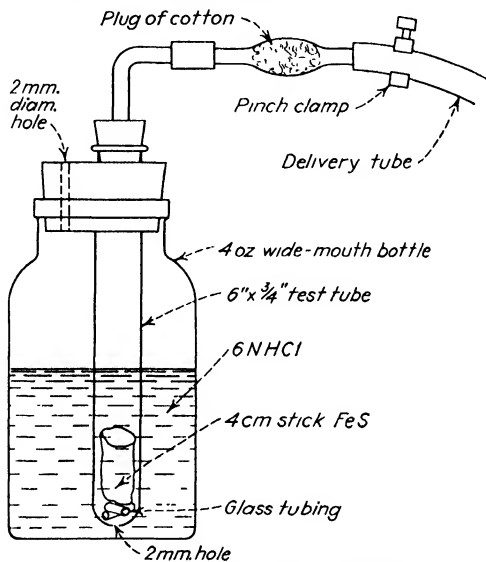


FIG. 7.—Hydrogen sulfide generator.

6-in. piece of rubber tube (delivery) equipped with a small screw clamp (see Fig. 7).

To operate the generator, put a couple of small bits of broken glass tubing into the 6-in. test tube, followed by a 4-cm. stick of ferrous sulfide. Fill the bottle half full of 6N hydrochloric acid and replace the stopper and its fittings. When hydrogen sulfide is desired release the clamp on the delivery tube; close the clamp when it is desired to stop the flow of gas.

An alternative method of generating hydrogen sulfide is by heating a mixture of 1 part paraffin and 3 parts of

powdered sulfur by weight with enough medium grade asbestos to make the mass porous. This requires only a 15-cm. Pyrex test tube (thin wall) fitted with a one-hole rubber stopper and delivery tube. The gas generation stops almost at once when heating is discontinued. However, as the apparatus sucks back on cooling, it is best to have a T tube in the delivery tube, and the finger tip should be held over the side outlet while using the generator and removed at once when heating is stopped.

A commercial mixture prepared for this type of generator and sold under the trade name "Aitchtues" can be purchased at very moderate prices from any of the standard chemical supply houses.

Capillary Delivery Tubes. The delivery tube used with the hydrogen sulfide generator must be of capillary dimensions in order to give the small bubbles desired—these being more completely absorbed than large bubbles. These delivery tubes are made by heating a 3-mm. glass tube for 3 to 4 cm. of its length until very soft, then removing it from the flame and quickly, but steadily, drawing it out into a capillary of about 1 mm. diameter. Finer capillaries are not convenient because they clog too easily. When cool, the tube is cut so that about 1 cm. of the original 3-mm. tube is left attached to about 7.5 cm. of capillary tubing. The thick end is used for attaching the capillary to the end of the rubber delivery tube on the generator and the capillary end for inserting into the liquid. At least six of these tubes should be prepared.

Reagent Droppers. In each desk there should be 1 doz. ordinary medicine droppers. Take *two* of these, and, using the technique described for the capillary delivery tubes, draw their tips out to capillaries, cutting off the capillary tip at a point where its external diameter is about $\frac{1}{2}$ mm. so as to leave the total length of the glass about 9 cm. These two droppers are very handy for transferring small quantities of reagents from one vessel to another.

Capillary pipettes are also useful for this same purpose. These pipettes are capillary tubes about 2 mm. in external diameter and 10 cm. long and are best prepared from 5 mm. soft-glass tubing as described above. The ends are *cautiously* fire-polished in a small flame. To use them, place one end of the tube in the liquid, press the tip of a finger over the upper end of the capillary, and lift the tube out. To empty the tube, hold it with the open end *slanted* downward, cautiously lift the finger tip off the other end, and allow the liquid to fall, drop by drop, into the container. About five of these pipettes should be made.

Stirring Rods and Spatulas. Stirring rods are made by cutting 5 in. lengths of 2-mm. glass rod, drawing one end out to 1 mm. diameter, and fire-polishing both ends. If no rods of this diameter are available, larger rods may be drawn out or else capillaries, prepared as if for capillary pipettes, may be sealed off at both ends and used as stirring rods.

Spatulas may be made by heating the small ends of stirring rods and pressing them flat between two flat metallic surfaces. The flattened ends should be small as they must reach the bottoms of the centrifuge tubes when used for the transfer of precipitates. About six stirring rods and four spatulas should be sufficient.

Reagent Containers. The usual liquid reagent containers have a capacity of, for those most used, about 30 ml. and, for the others, about 2 to 8 ml. The 30-ml. containers, about 15 in number, may be the usual 1-oz. dropping bottles equipped with rubber bulbs. These may be placed in holes drilled in a wooden block to keep them in a convenient unit. The other reagents, about 65 in number, are in vials arranged in alphabetical order in a similar block. Each vial is fitted with a one-hole cork through which a 3-mm. glass tube extends to within 1 mm. of the bottom of the vial, sufficient projection of the tube above the cork being left to allow the tube to be used as a pipette.

A small V-shaped groove may be cut vertically in the cork to act as an air vent.

Gas Evolution Apparatus. Using the narrow width of a flame obtained from a wing-top burner, strongly heat a

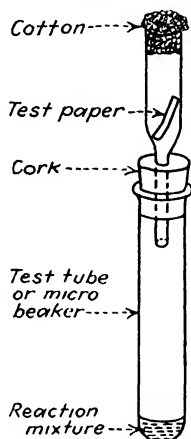


FIG. 8.--Gas evolution apparatus.

piece of 10-mm. glass tubing, and draw it down to a diameter of about 2 or 3 mm. Cut the tube so that about 2.5 cm. of the narrow portion remains attached to 2.5 cm. of the thicker portion. Put the narrow portion through a one-hole rubber stopper fitted in a 4-in. test tube (Fig. 8).

PART II

THEORY OF ANALYSIS

IMPORTANT PRINCIPLES

Introduction. It is perfectly possible for a student to perform the laboratory portion of a course in qualitative analysis without knowing many of the laws and principles of chemistry. The usual unknown is made up using concentrations that fall between certain definite limits, and the instructions are so written as to give good results with such unknowns. In practical work, however, the unknowns may vary far beyond these limits. Consequently, it becomes more and more necessary that the analyst know the theories that were used in making up this procedure so that he can vary his tactics whenever he finds it necessary. A knowledge of the laws and principles is what makes the difference between the good and the poor analyst.

As a rule, the analytical student makes use of these laws in laboratory work long before they are reached in the lecture. It is almost impossible to correlate the laboratory and lecture properly. For this reason a brief, qualitative review of the more important principles will be given here with the expectation that they will be expanded in the lecture portion of the course.

Concentration Units. It has already been stated that practically all of analysis deals with solutions. Analysis is not absolute in nature. If a large granule of lead nitrate is dissolved in 1 ml. of water, the presence of lead in the solution is easily demonstrated by using the proper reagents. If, however, 1 drop of this solution is added to 1000 liters of pure water, the resulting solution will be so dilute that

we can not detect the presence of the lead—although it is certainly there. The only difference between these two solutions is one of *concentration*, and we shall find that the concentrations of reagents may have just as much to do with the results of an analysis as do the concentrations of the ions for which we are testing. In order, therefore, for us to give—and to understand—instructions, it is important that we define two units in terms of which we can conveniently express the concentrations of our solutions.

These are based on the number of mols or the number of equivalent weights of the material in a liter of solution. A solution that contains 1 gram-molecular weight (*i.e.*, 1 mol) of solute in 1 liter of *solution* is a 1*M* (one molar) solution; one that contains 2 gram-molecular weights of solute in 1 liter of solution is a 2*M* (two molar) solution; etc.

A solution that contains 1 gram-equivalent weight of solute per liter of *solution* is a one normal (1*N*) solution; etc. For example, a solution containing 231.6 g. of lead nitrate, $\text{Pb}(\text{NO}_3)_2$, per liter of solution is a 1*M* (or 2*N*) solution. A solution containing 36.5 g. of hydrochloric acid per liter of solution is both a 1*M* and a 1*N* solution. A solution of hydrochloric acid containing 18.25 g. per liter is a half-normal (0.5*N*) or a half-molar (0.5*M*) solution.

To comprehend this, it is necessary to understand how to determine the equivalent weight of any compound. In most cases, it is only necessary to divide the gram-molecular weight of the compound by the total valence of that radical in the molecule that is most important to the reaction that is to be carried out. For example, in acids, it is usually the hydrogen ion that is the most important; in bases, it is the hydroxyl radical; in sodium sulfate, Na_2SO_4 , it may be the sodium or it may be the sulfate; in $\text{K}_2\text{Al}_2(\text{SO}_4)_4$, it may be either the potassium, the aluminum or the sulfate radicals. It all depends upon whether the substance is to be used as a source of hydrogen, hydroxyl, sodium, aluminum, potassium, sulfate, or other ion. For example, using

the compound $K_2Al_2(SO_4)_4$, if the solution is to be used for precipitating some salt of potassium, the equivalent weight is found by dividing the gram-molecular weight by two—since there are two valences represented by the potassium in each molecule of the compound. If it is to be used as a source of aluminum (as in the precipitation of aluminum hydroxide), the gram-molecular weight must be divided by six. As a source of sulfate radical, the gram-molecular weight must be divided by eight—since that is the total number of valences represented by the sulfate radicals present.

Other methods of expressing concentrations are sometimes used, *e.g.*, grams per liter or per 100 ml. (milliliters) of the *solvent*, percentage by weight or volume (parts per hundred), parts per million by weight, etc. These are, however, rarely used in qualitative analysis though they are often used in quantitative work.

Calculations Involving Normalities. In the previous section the method was given for the preparation of solutions of given normalities from the pure substances and water. Often, however, it happens that a solution of high, known concentration is available but a solution of lower concentration is needed. It is possible to dilute such solutions to the lower concentration more rapidly than to weigh out the required solute.

For example, let it be assumed that 24 drops of a $3N$ solution of sulfuric acid is needed. The ordinary concentrated sulfuric acid is approximately $36N$, and it is desired to find out how to dilute it in order to get the concentration and volume of acid needed. There is an important formula which applies to all such problems, *i.e.*,

$$N_1 \times V_1 = N_2 \times V_2$$

where N_1 is the normality and V_1 is the volume of the original solution used; N_2 is the normality, and V_2 is the

volume the solution will have after dilution. Using this formula in the above problem,

$$\begin{array}{ll} N_1 = 36 & N_2 = 3 \\ V_1 = ? & V_2 = 24 \text{ drops} \end{array}$$

Therefore,

$$\begin{aligned} 36 \times V_1 &= 3 \times 24 \\ V_1 &= 7\frac{2}{3} = 2 \text{ drops} \end{aligned}$$

This means that 2 drops of concentrated sulfuric acid must be *diluted to* 24 drops (by adding water) to make 24 drops of 3*N* sulfuric acid.

In the Appendix there is given a list of the normalities of the common concentrated acids and bases for use in these calculations. It must be remembered that these figures are not exact, for the concentrations of the original concentrated reagents may vary in strength. However, the results obtained are sufficiently close for use in *qualitative* analysis—though far too inaccurate for use in quantitative work.

The above equation also applies to volumetric reactions between ions in solution. For example, if it is desired to calculate the volume of 2*N* sulfuric acid required to neutralize 50 drops of 3*N* ammonium hydroxide, one again substitutes in the formula,

$$\begin{array}{ll} N_1 = 2 & N_2 = 3 \\ V_1 = ? & V_2 = 50 \text{ drops} \end{array}$$

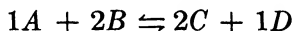
Therefore,

$$\begin{aligned} 2 \times V_1 &= 3 \times 50 \\ V_1 &= 75 \text{ drops} \end{aligned}$$

This gives the answer not only to *this* problem but also tells us that 50 drops of *any* 3*N* base will require 75 drops of *any* 2*N* acid for neutralization.

General Principles. Although many different laws and phenomena will be studied during the course, it will be found that there are two principles that will be applicable to every case. These are the law of mass action and Le Chatelier's principle.

The *law of mass action* states that in any chemical reaction the mathematical product of the concentrations of the products of the reaction divided by the product of the concentrations of the reacting substances will, when the reaction has attained equilibrium, equal a constant K regardless of what concentrations were used at the beginning. This constant will never vary unless the *temperature* at which the reaction is carried out is changed. To illustrate this law let us assume that two substances, A and B react to form C and D ; *e.g.*,



If this reaction is allowed to stand until it has attained equilibrium and an analysis is carried out for each substance, it will be found that the following relationship will hold true

$$\frac{(C)(C) \times (D)}{(A) \times (B)(B)} = \frac{(C)^2 \times (D)^1}{(A)^1 \times (B)^2} = K$$

where (A) , (B) , etc., represent molar concentrations. If to that same mixture some more of either A , B , C , or D is added, equilibrium is established, and an analysis is again carried out, it will be found that the same relationship gives the same constant—if the temperature is kept the same as before.

Le Chatelier's principle states that, if a stress is applied to a system in equilibrium, the equilibrium will shift in such direction as to reduce the stress. In chemistry there are many ways of applying stress to a system. Changes in concentration, pressure, temperature, intensity of illumi-

nation, etc., are common examples. As an illustration let us assume that the following reaction is taking place.



According to the law of mass action, the relationship

$$\frac{(\text{NH}_3)(\text{NH}_3)}{(\text{N}_2) \times (\text{H}_2)(\text{H}_2)(\text{H}_2)} = \frac{(\text{NH}_3)^2}{(\text{N}_2) \times (\text{H}_2)^3} = K$$

will hold true. According to Le Chatelier's principle, if a stress is applied to the system, the reaction will shift in such manner as to remove the stress. If the mixture is heated, the reaction will shift to the *left* so as to *remove* heat; if the mixture is subjected to increased pressure, the reaction will shift to the *right* since that is the direction which will decrease the volume of the gases as well as the pressure. Increasing the concentration of either hydrogen or nitrogen will shift the reaction to the right, using up these gases in the production of ammonia. On the other hand, increasing the concentration of ammonia or removing nitrogen will shift the reaction to the left, etc. Similarly, any chemical equilibrium can be shifted by applying the proper stress.

Electrolytes and Nonelectrolytes. Soon after the development of the voltaic battery, it was discovered that certain substances in water solution are excellent conductors of electricity. To distinguish this conductor from metallic conductors, the former are known as *electrolytic conductors* or *electrolytes*. In general, all salts, acids and bases are electrolytes.

Another class of compounds is known as the *nonelectrolytes*. To this class belong such substances as sugar,

* The volume relationships indicated here follow from Gay-Lussac's law of combining volumes. This law states that *in reactions between two or more gases, the ratio of the volumes of the gases undergoing reaction is expressible in small, whole numbers*. It should be reviewed by the student, using any good inorganic text.

alcohol, acetone, etc., which are characterized by the fact that their aqueous solutions are nonconductors of electricity.

The first successful attempt to explain the differences between electrolytes and nonelectrolytes was made by the Swedish chemist, Arrhenius (63)* late in the nineteenth century. His theory postulated that the chief difference between an electrolyte and a nonelectrolyte is that the molecules of electrolytes break up, in solution, into two or more radicals (atoms or groups of atoms which act as a unit in a chemical reaction) each carrying its own characteristic positive or negative charge. These charged particles, known as *ions*, act as the carriers of electricity when a solution is undergoing electrolysis.

One of the most important characteristics of solutions of electrolytes is expressed in the *additivity* principle. The aqueous solution of any given electrolyte has properties which are the sum of the properties characteristic of each kind of ion present in the solution. For example, a solution of cupric dichromate gives a yellow precipitate with lead nitrate solution and a red-brown precipitate with silver nitrate solution. It oxidizes acid solutions of bromides giving bromine, and oxidizes many organic compounds to form highly colored substances. These, and many other properties of cupric dichromate solution, are characteristic of solutions of all dichromates and may therefore be considered the properties of dichromate ions.

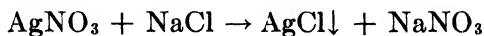
Similarly, when cupric dichromate is treated with sodium sulfide, a black precipitate forms; with excess ammonium hydroxide a deep blue color forms; and with $K_4Fe(CN)_6$ solution a reddish solid precipitates. These are characteristics of all solutions containing cupric ions.

These two sets of properties together make up the properties of cupric dichromate. Even the brown color of cupric dichromate solutions is the result of a combina-

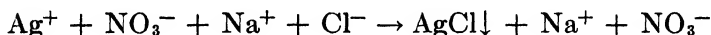
* The numbers in the parenthesis throughout the text are code numbers under which the references on the subject may be found in the Appendix.

tion of the blue of the cupric ions and the orange of the dichromate ions.

Since the chemical properties of a solution of an electrolyte are due chiefly to the individual ions present, it is evident that chemical reactions between solutions of electrolytes must be, essentially, reactions between ions. To be accurate, therefore, reactions between such solutions should be written in terms of ions instead of molecules. For example, the reaction between silver nitrate and sodium chloride solutions to form insoluble silver chloride is usually written



It is more properly written



This equation shows that the only reaction occurring is one between silver and chloride ions to form silver chloride. The sodium and nitrate ions remain in the solution, unchanged.

The above equation is called an *ionic* equation.

Strong and Weak Electrolytes. Experimentally it is found that electrolytes vary as to the ease with which they conduct electricity. Hydrochloric acid, for example, is an excellent conductor of electricity while acetic acid is much poorer.* This is owing to the fact that while some electrolytes are highly ionized, *i.e.*, most of the molecules placed in solution are broken up into ions; others, like acetic acid, ionize to a much less extent—in other words,

* Recent theories by Debye, Hückel, and others postulate that such strong electrolytes as sodium chloride and potassium chloride are *completely ionized*, even in the most concentrated solutions. Although concentrated solutions of strong electrolytes behave as if the solute were only partly ionized, modern theories explain this on the basis of probable mutual interference of ions of opposite charge on each other's movements. This theory will be discussed more fully later (p. 63).

only a few of the molecules ionize, the rest remaining in solution as whole molecules.*

It has been found that both the law of mass action and Le Chatelier's principle apply to solutions of weak electrolytes. Taking the weak electrolyte, acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, for example, we set up the following equation (letting Ac stand for $\text{C}_2\text{H}_3\text{O}_2$ and Ac^- for *acetate ion*):



According to the principle of Le Chatelier, if we add Ac^- to the solution, we should cause H^+ and Ac^- to combine, the result being that the hydrogen ion concentration should diminish and the HAc concentration (the concentration of acetic acid molecules) should increase. This is exactly what occurs if we add sodium or ammonium acetate to the solution. The addition of H^+ (which can be accomplished by adding any strong acid, such as HCl) should cause a decrease in the concentration of Ac^- and again an increase in the concentration of HAc molecules. These are examples of the *common-ion effect*.

This is further brought out by applying the law of mass action.

In the expression

$$\frac{(\text{H}^+) \times (\text{Ac}^-)}{(\text{HAc})} = K_a$$

(K_a for HAc at 18°C . is 1.8×10^{-5}) it is easily seen that if K_a (the *ionization* or *dissociation constant*) is to remain the same for all such solutions of acetic acid, an increase in the concentration of Ac^- must result in a decrease in the

* This is true only of ordinary solutions, however. As the concentration of any weak electrolyte is lowered, it is found that the conductivity of the solution (measured in a cell arranged to keep the *whole solution* between the electrodes) is increased, reaching a maximum at infinite dilution. Arrhenius explained this by assuming that at infinite dilution ionization is always complete, *i.e.*, in such solutions none of the solute is present in the form of molecules. Later experiments have verified this conception.

concentration of H^+ and an increase in the concentration of HAc . If this were not true, the fraction would have a larger value than K_a —which is not the case.

The same relationship holds true for weak bases. NH_4OH , for example, dissociates as follows:



Setting this up in the form used for acetic acid,

$$\frac{(NH_4^+) \times (OH^-)}{(NH_4OH)} = K_b$$

The same rule will apply to this equilibrium as applied to the acetic acid equilibrium. The *dissociation* (or *ionization*) *constant* for NH_4OH at $18^\circ C$. is 1.75×10^{-5} .

To increase the concentration of one ion in a solution without adding the other ions also, it is only necessary to choose a highly soluble strong electrolyte which contains the ions desired and add it to the solution. As salts in general are, with very few exceptions, strong electrolytes, they are the most commonly used for this purpose.

A solution of an acid containing a high concentration of a salt of a weak acid or of a base containing a high concentration of a salt of a weak base is called a *buffer* solution. The value of such solutions lies in the fact that fairly large quantities of acids or bases can be added to them without much change in the hydrogen or hydroxyl ion concentration of the solution. The concentrations of these ions will be low, but quite constant. This makes such solutions invaluable where changes in the acidity of the solution are undesirable and much use is made of buffering agents (such as ammonium acetate, ammonium chloride, sodium acetate, etc.) throughout the analytical procedure.

Strong electrolytes are somewhat different from weak electrolytes. Without great error, 1 gram-molecular weight of HCl dissolved in water may be considered to break up

completely, even in concentrated solutions, to give 1 gram-molecular weight of H^+ (1 *gram-ion* of hydrogen) and 1 gram-molecular weight of Cl^- . On the basis of this assumption, the reaction goes to completion as indicated by the equation

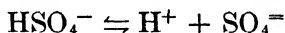


Consequently, a 1*M* solution of HCl contains 1 gram-ion per liter each of H^+ and Cl^- . Similarly, a 1*M* solution of NaOH (a strong electrolyte) contains 1 gram-ion per liter each of Na^+ and OH^- .*

The case of a strong di- or tri-basic acid or base is not quite so simple, however. These substances ionize in steps, in the first step acting as strong electrolytes but in the latter stages acting as increasingly weak electrolytes. Sulfuric acid, for example, ionizes in the first stage as follows, the ionization going to completion:



The bisulfate ion then undergoes ionization, this step, however, being reversible as in the case of weak electrolytes:



Consequently, sulfuric acid exhibits properties intermediate between those of strong and of weak electrolytes.

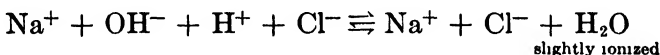
In general, experiment has shown that salts, with the exception of compounds of lead, tin, mercury, some zinc compounds, and one or two less known types, are all strong electrolytes. The hydroxides of the alkali and the alkaline earth family, and the three common acids, sulfuric, nitric, and hydrochloric, are also strong electrolytes.

* Tables of apparent degrees of ionization as calculated from conductivity measurements list strong electrolytes such as hydrochloric acid and sodium hydroxide as being only 90 per cent ionized in 0.1 *M* solutions. The more modern theories, however, justify treating them as being completely ionized. (See Debye-Hückel theory.)

On the other hand, ammonium hydroxide, acetic acid, hydrosulfuric acid, benzoic acid, and the salts noted above as exceptions are all classed as weak electrolytes. It must be remembered, however, that there is no sharp line of division between strong and weak electrolytes, as compounds are known ranging through all degrees from the weak to the strong.

Hydrolysis. One of the important consequences of the characteristic reactions of weak electrolytes is found in the way certain acids and bases react with each other as well as the way certain salts react with water.

Neutralization is commonly defined for beginning students as being the reaction between any acid and base to form a salt and water. On writing the ionic equation for a neutralization, however, it soon becomes evident that the reaction is more accurately defined as being a reaction between hydrogen ions and hydroxyl ions to form water, *e.g.*, the reaction between HCl and NaOH is



Even in pure water, however, ionization takes place to some extent, forming H^+ and OH^- . In pure water the concentration of H^+ is 10^{-7} g. or 10^{-7} mol per liter; while that of the OH^- is 17×10^{-7} g. or 10^{-7} mol per liter. Consequently, any solution containing equal mol concentrations of H^+ and OH^- is *neutral*. On the other hand, if the mol concentration of H^+ is greater than the mol concentration of OH^- , the solution is acid; if the mol concentration of OH^- predominates over that of the H^+ ions, the solution is basic.

Owing to the fact that water is an electrolyte (though a *very weak* one) we find that, with certain types of salts, the *reverse* of neutralization will occur. For example, if pure NaAc is dissolved in water a slight reaction will occur.

ions found in every aqueous solution. Its equilibrium expression may be set up as follows:

$$\frac{(\text{H}^+) \times (\text{OH}^-)}{(\text{H}_2\text{O})} = K \quad (1)$$

This can be re-written as follows:

$$(\text{H}^+) \times (\text{OH}^-) = K \times (\text{H}_2\text{O}) \quad (2)$$

It can be shown by a few simple calculations that the concentration of water molecules in ordinary solutions is not greatly different from that in pure water—in other words, it remains practically constant. If this is assumed to be true, the product $K \times (\text{H}_2\text{O})$ may be set equal to another constant, and the following expression results:

$$(\text{H}^+) \times (\text{OH}^-) = K_w \quad (3)$$

In pure water the concentration of H^+ , as determined experimentally at $25^\circ\text{C}.$, is 0.0000001 g. per liter and of OH^- is 0.0000017 g. per liter. If these are expressed in terms of mols, the concentration of each of H^+ and OH^- is 10^{-7} mol per liter. Substituting in Equation (3),

$$\begin{aligned} 10^{-7} \times 10^{-7} &= K_w \\ \therefore K_w &= 10^{-14} \end{aligned}$$

Consequently, for aqueous solutions at $25^\circ\text{C}.$,

$$(\text{H}^+)(\text{OH}^-) = 10^{-14} \quad (4)$$

When an acid is added to water the hydrogen ion concentration is increased. However, no matter how high the concentration of hydrogen ions may be, there will be some hydroxyl ions yet remaining in the solution. Conversely, an alkaline solution always contains some hydrogen ions. If the concentration of one of the ions is known, the concentration of the other may be calculated by making use of the final equilibrium expression [Equation (4)]. For

example, the hydrogen ion concentration in a solution containing 10^{-2} mol of hydroxyl ions per liter is

$$(H^+)(10^{-2}) = 10^{-14}$$

$$(H^+) = \frac{10^{-14}}{10^{-2}} = 10^{-12} \text{ mol per liter}$$

From this it can be seen that the alkalinity or acidity of any aqueous solution can be expressed in terms of the

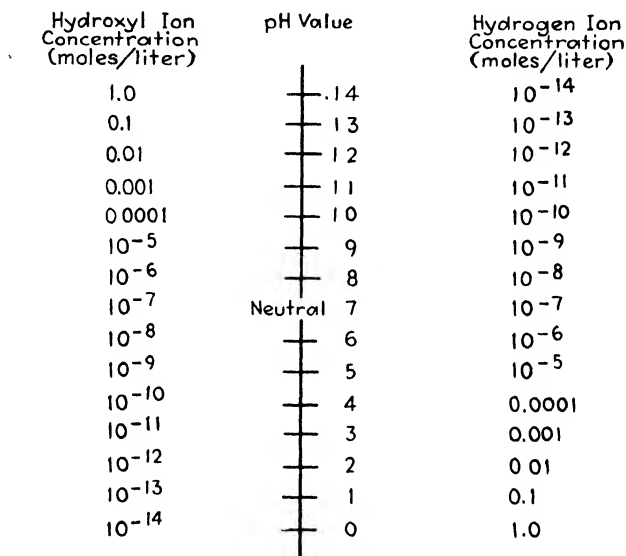


FIG. 9.—Chart of pH values and ion concentrations.

hydrogen ion concentration alone. A solution is said to be acid, neutral, or basic according to whether the hydrogen ion concentration is greater than, equal to, or less than 10^{-7} mol per liter.

Often it is more convenient to express the hydrogen ion concentration of a solution in terms of the log of the reciprocal of the hydrogen ion concentration, *i.e.*, in terms of the pH ("potential hydrogen") of the solution. For example, if the hydrogen ion concentration of a certain

solution is 10^{-4} mol per liter, the pH of the solution is given by the following:

$$\text{pH} = \log \frac{1}{(\text{H}^+)} = \log \frac{1}{(10^{-4})} = 4$$

A neutral solution, therefore, has a pH of seven; a solution having a pH smaller than seven is acid, while one whose pH is greater than seven is basic (see Fig. 9).

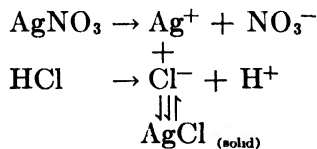
Solubility Product: Supersaturation. Before starting a discussion of precipitation reactions and the problems peculiar to them, it is necessary that the student gain some new conceptions concerning solubilities and saturated solutions. Often, during beginning chemistry, different substances are characterized as being "soluble" or "insoluble." Properly speaking, there is no such thing as a *completely* insoluble substance. A substance may be so insoluble that it is impossible for us to detect its presence in solution by any chemical means available at present; nevertheless, some small quantity is probably present in the dissolved state. This is especially true of the common so-called insoluble salts such as AgCl , CuS , CaCO_3 , and many others. It can be definitely shown that these salts are soluble—to a very slight extent, of course, but soluble, nevertheless.

To understand what is meant by the term *solubility*, it is first necessary that a saturated solution be defined. A *saturated solution* is a solution in which the dissolved material is in equilibrium with excess undissolved material. This is best explained by describing what happens during the preparation of a saturated solution. If one places a lump of sugar in water, molecules of sugar immediately begin to pass into solution. At first, this is the only thing that occurs, but, as soon as a few molecules are in solution, some of them will, in moving about, collide with other sugar molecules and precipitate out again. This precipitating process is slow at first, but, as the concentration of dissolved

molecules increases, collisions between molecules will become more and more frequent until finally a point will be reached when sugar is precipitating at exactly the same rate as the sugar is dissolving. When this point is reached, it appears to the observer that no more sugar is dissolving. Actually, these two opposing actions are continuing all the time, but the net result is that the solid left in the mixture will neither increase nor diminish in quantity since material is precipitated as fast as it is being dissolved. The dissolved molecules are therefore in equilibrium with undissolved material and the solution is now saturated.

With this picture in mind, we can define the term *solubility*. The *solubility* of a substance is the concentration of its *saturated* solution at a given temperature. As a rule, the solubility of a substance increases with increased temperature. Therefore, solubility tables usually give the values of determinations made at temperatures varying from 15 to 25°C.

If these concepts are remembered, it is possible to take up the problem connected with the formation and re-solution of precipitates. One of the first precipitation reactions studied in the laboratory is the formation of silver chloride by the addition of a solution of chloride ions to a solution of some silver salt. The reaction is essentially a reaction between silver ions and chloride ions to form silver chloride, *e.g.*,



Since HNO_3 is a strong electrolyte, there is little tendency for combination of its ions. Precipitation of AgCl occurs leaving a solution saturated with respect to Ag^+ ions and Cl^- ions and in equilibrium with solid AgCl . Con-

sequently, the law of mass action applies and the following expression holds true:

$$\frac{(\text{Ag}^+) \times (\text{Cl}^-)}{(\text{AgCl})_{(\text{solid})}} = K'$$

By using a few justifiable assumptions, it is possible to simplify this expression to the following form:

$$(\text{Ag}^+) \times (\text{Cl}^-) = K_{s.p.}$$

$K_{s.p.}$ is known as the *solubility product constant* while the mathematical product, $(\text{Ag}^+) \times (\text{Cl}^-)$, is known as the solubility product. This simply means that, no matter whence the ions come, if, after equilibrium between solid and dissolved material is attained, the concentration of the silver ions remaining in solution, in mols per liter, is multiplied by the concentration of the chloride ions, the resulting product can never be greater than the value of the solubility product constant for silver chloride. In a saturated solution of silver chloride, this product will exactly *equal* the solubility product constant.

It can be seen from this illustration that the so-called *common-ion effect* applies to this equilibrium, *i.e.*, the greater the concentration of Cl^- , the smaller will be the concentration of Ag^+ left in solution and the more complete the precipitation.

Each slightly soluble electrolyte has its own solubility product constant. At 18°C ., the constant for AgCl is 2×10^{-10} , for AgI , 1×10^{-16} , etc.

For more complicated molecules the relationship becomes a little more complicated. For example, the expression for PbCl_2 is

$$(\text{Pb}^{++}) \times (\text{Cl}^-)^2 = K_{s.p.} = 1.0 \times 10^{-4} \text{ (at } 25.2^\circ\text{C.)}$$

and for $\text{Pb}_3(\text{PO}_4)_2$

$$(\text{Pb}^{++})^3 \times (\text{PO}_4^{=})^2 = K_{s.p.} = 8 \times 10^{-43} \text{ (at } 25^\circ\text{C.)}$$

Therefore, the solubility product principle states that, in a saturated solution of any slightly soluble electrolyte, the mathematical product of the molar concentrations of the ions of the substance, each concentration raised to a power equal to the number of those ions in the molecule, will equal a constant, provided the *temperature* remains constant. A given constant will, in general, hold true only for:

1. One particular temperature. Most substances have higher solubility product constants at higher temperatures.
2. One particular solvent.
3. One particular *slightly soluble electrolyte*.
4. A saturated solution, *i.e.*, a solution in which undissolved material is in equilibrium with its dissolved ions.
5. One particular pressure. This applies to slightly soluble gases such as hydrogen sulfide. Figures are usually given for one atmosphere pressure.
6. Solutions whose total electrolyte concentration is low (see Salt Effect, page 62).

Occasionally one will find a case where ions are mixed in such concentration as to exceed the solubility product, yet no precipitation occurs. Such solutions are in a metastable state and will often remain that way for some time unless some disturbing factor is introduced. A solution that contains more solute in solution than its saturated solution would contain at that temperature is called a *supersaturated* solution.

Most of the identification tests used in qualitative analysis depend upon the formation of precipitates, many of which readily give supersaturated solutions. Consequently, it is important to know the methods available for bringing about the precipitation of such substances. Some of the more common of these methods are:

1. Scratching or rubbing the inside wall of the vessel with a stirring rod. This is the best method to use in analysis.

2. Sudden chilling of a supersaturated solution will often cause precipitation to occur.

3. Heating the solution slightly will, in some cases, cause precipitation to occur.

4. Shaking the solution will often disturb the metastable state existing in the solution and cause precipitation.

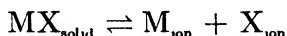
Colloidal Solutions. Occasionally, it will be found that, on addition of a reagent to an unknown, a solid material forms but refuses to settle out. The solid material is so finely divided that no individual particle possesses enough weight to cause it to go to the bottom, even in the centrifuge. Since the analysis depends on being able to separate this solid material from the filtrate, it is important that some method be devised to precipitate colloids.

Colloidal solutions consist of extremely fine particles suspended throughout the liquid. Each of the particles carries a variable number of electrical charges, all the particles in a given colloidal solution having the same polarity. The fact that the charges on all the particles are of the same sign results in their repelling each other so that they cannot collect into the larger particles necessary for settling. This suggests that if these charges could be neutralized precipitation would occur. It is often possible to neutralize these charges by adding ions carrying a charge opposite in nature to those carried by the colloidal particles. Unfortunately, one can never add a negative ion without adding a positive ion at the same time—for ions do not exist in groups so that we can add one kind at will. However, it happens that a bivalent ion is much more effective than two monovalent ions. Consequently, one can precipitate a positive colloid by adding ammonium sulfate, the bivalent negatively charged sulfate ion being much more effective than the positively charged monovalent ammonium ions. Similarly, calcium chloride would be a good precipitant for negative colloids.

Unfortunately, these compounds cause precipitation of certain metals in the wrong place and add ions for which we must test later. However, a high concentration of ammonium nitrate will usually precipitate any colloid, though it may be a slow process. Magnesium sulfate is one of the best general colloid precipitants but may be used only when neither of its ions will interfere with the analysis.

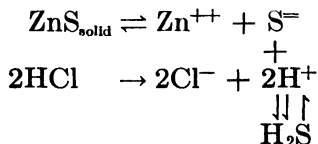
Usually, heating a colloidal solution will cause it to precipitate. The heat tends to remove the charges on the particles, and the internal agitation that accompanies the heating causes the particles to collect in masses sufficiently large to insure settling.

Dissolving Precipitates. It has already been pointed out that a saturated solution of any substance is simply an example of an equilibrium between solid material and its ions in solution. Therefore, the problem of putting a solid material into solution resolves itself into a question of the possible ways one can force the reaction.



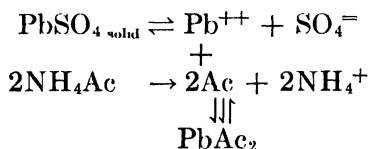
to the right. There are several ways this can be done.

1. If one of the ions can be forced to react with some other ion to form a slightly soluble gas which will escape and thus remove that ion from the reaction mixture, the reaction will proceed to the right and the solid will dissolve. When ZnS is treated with HCl it will dissolve owing to the fact that H_2S , being only slightly soluble in acid, removes the S^- ion as fast as the latter is formed.

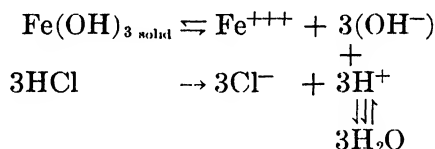


2. Occasionally, one of the ions can be caused to react with the ions from some reagent to form a weak electrolyte

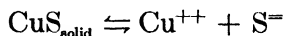
(such as water). When the slightly soluble PbSO_4 is treated with a strong solution of ammonium acetate, the PbSO_4 will dissolve. This is due to the reaction between the Pb^{++} and acetate ions to form the slightly dissociated PbAc_2 , the latter being one of the few salts that are *weak* electrolytes.



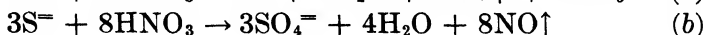
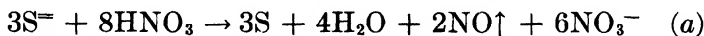
An example of a reaction in which the formation of water from one of the ions causes the reaction to go to completion and the precipitate to dissolve is the case of ferric hydroxide dissolving in hydrochloric acid.



3. Destruction of one of the kinds of ions produced will shift the equilibrium and cause the solid to go into solution. Copper sulfide, for example, is not soluble in hydrochloric acid but *is* soluble in warm 3*N* nitric acid. This is owing to the fact that the nitric acid oxidizes the sulfide ions to free sulfur and sulfate ions. The reaction might be written as follows:

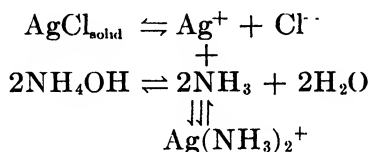


The sulfide ion is removed by the following reactions:

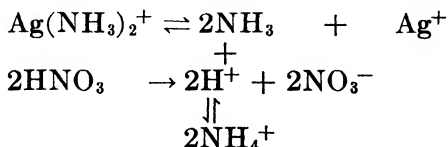


As fast as sulfide ion goes into solution, it is destroyed in these two simultaneous reactions.

4. If a reagent is added which causes the formation of a complex ion, the reaction will proceed towards the right. A *complex ion* is an ion formed by the combination of a simple ion with other ions or with neutral molecules. Examples of these are the cupric ammonium ion, $\text{Cu}(\text{NH}_3)_4^{++}$; the silver ammonium ion, $\text{Ag}(\text{NH}_3)_2^+$; the cuprocyanide ion, $\text{Cu}(\text{CN})_3^-$; the cobalticyanide ion, $\text{Co}(\text{CN})_6^{=}$; the zinc ammonium ion, $\text{Zn}(\text{NH}_3)_4^{++}$; and many others of like nature. An example of forming complex ions in order to put a substance into solution is the use of ammonium hydroxide to dissolve AgCl . The reaction that occurs is as follows:

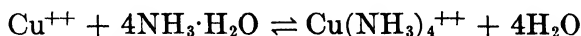


The complex ions, which are stable and dissociate only slightly to give simple ions, have entirely different properties than the simple ions from which they were formed. Therefore, the above reaction removes Ag^+ from the mixture and the AgCl goes into solution. Acidification of this mixture will reprecipitate the AgCl , because the NH_3 is removed, as is shown in the following equation:



Complex Ions. Many metallic ions combine with certain types of neutral molecules or with anions to form complex ions, some of which are exceedingly important. A few of these were mentioned in the preceding paragraphs.

The cupric ammonium ion, $\text{Cu}(\text{NH}_3)_4^{++}$, is formed by the combination of Cu^{++} with four NH_3 molecules. The reaction* may be written

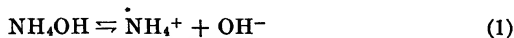


Similarly, the cobalticyanide ion is formed by the combination of cobaltic ions with cyanide ions:



Many of these complex ions are used in the analytical separation of the metals. A few of those not mentioned previously are the ammonia complexes of cadmium, cobalt, and nickel, $\text{Cd}(\text{NH}_3)_4^{++}$, $\text{Co}(\text{NH}_3)_6^{++}$ and $\text{Ni}(\text{NH}_3)_4^{++}$; the chloride complexes of lead, mercury, antimony, and tin, PbCl_4^- , HgCl_4^- , SbCl_6^- , and SnCl_6^- ; and the thio complexes of arsenic, antimony, and bismuth, examples of which are the thioarsenite, AsS_3^- ; thioantimonate, SbS_3^- ; and thiostannate, SnS_3^- , ions. The ammonia complexes are formed by treating solutions of the metallic ions with excess ammonium hydroxide; the chloride complexes exist in strong hydrochloric acid solutions of lead, mercury, antimony, and tin ions; and the thio complexes form when the sulfides of arsenic, antimony, or tin are treated with solutions of sodium or ammonium sulfide.

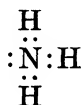
* Although a solution of ammonia in water is usually considered to be a solution of NH_4OH molecules, many of its reactions, as well as many spectral and other physical data, indicate that it is chiefly a solution of simple NH_3 molecules. Consequently, its characteristic reactions may be explained by the existence, in ammonium hydroxide, of two equilibriums:



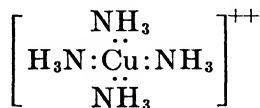
Equation (1) represents its weakly basic reactions, while Equation (2) shows that a solution of ammonium hydroxide may yield a high concentration of NH_3 molecules.

The phenomenon of ions combining with other ions or neutral molecules to form complex ions is not explained by ordinary conceptions of valence. A broader theory was developed, therefore, by A. Werner, postulating the existence of two types of valence. The first of these, the *primary* valence, is the ordinary kind of chemical valence. The second, which Werner termed the *auxiliary* or *secondary* valence, is a type of bond which an ion can exhibit in addition to its ordinary valence.

The reason for the existence of secondary valence is not fully understood as yet. However, it is believed that in many cases the secondary valence (sometimes called the *coordinate* valence) is due to the ability of ions or neutral molecules to attach themselves to unused electron pairs in other ions or neutral molecules. For example, the valence-electronic configuration of the ammonia molecule might be written,



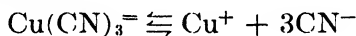
where the dots represent electrons, the hydrogen atoms being held to the nitrogen through shared electron pairs. The unshared pair of electrons makes this molecule readily capable of forming complex ions. For example, the configuration of the cupric ammonium ion may be written:



The maximum number of ions or neutral molecules with which a given ion can combine is called the *coordination number* of that ion. By studying these, it is possible to predict, with fair accuracy, the probable formula of any of the common complex ions. The coordination numbers of a few ions are given in the following table:

| | | | |
|-----------------------|---------|-------------------|---|
| Ag ⁺ | 2 | Hg ⁺⁺ | 4 |
| Cd ⁺⁺ | 4 | Mn ⁺⁺ | 6 |
| Co ⁺⁺ | 6 | Ni ⁺⁺ | 6 |
| Co ⁺⁺⁺ | 6 | O | 3 |
| Cu ⁺ | 2 and 3 | Pt ⁺⁺⁺ | 6 |
| Cu ⁺⁺ | 4 | Sb ⁺⁺⁺ | 6 |
| Fe ⁺⁺ | 6 | Sn ⁺⁺⁺ | 6 |
| Fe ⁺⁺⁺ | 6 | | |

The usefulness of complex ions depends upon the fact that, like weak electrolytes, *the complex body is in equilibrium with its simple components*. For example, the cuprocyanide ion in solution is in equilibrium with cuprous ions and cyanide ions:



Similarly, the cadmium cyanide ion sets up the following equilibrium:



For each of these equilibria, it is possible to write an equation similar to the expression used for weak electrolytes:

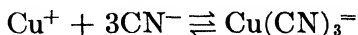
$$\frac{(\text{Cu}^+)(\text{CN}^-)^3}{(\text{Cu}(\text{CN})_3^-)} = K_{\text{Cu}(\text{CN})_3^-} = 5 \times 10^{-28}$$

$$\frac{(\text{Cd}^{++})(\text{CN}^-)^4}{(\text{Cd}(\text{CN})_4^{--})} = K_{\text{Cd}(\text{CN})_4^{--}} = 1.4 \times 10^{-17}$$

The dissociation or *instability constants* for different complex ions have different values. The smaller the constant, the lower will be the concentration of simple ions existing in the solution of a given complex ion.*

* Particular attention might be called to the use of CN^- ion in the separation of copper and cadmium. In solutions of the cyanide complexes of cadmium and copper, the concentration of the simple ions is sufficiently great for both CdS and CuS to be precipitated by treatment with H_2S . The dissociation constant of the $\text{Cu}(\text{CN})_3^-$, however, is much smaller than that of the $\text{Cd}(\text{CN})_4^{--}$. Consequently, by putting in excess KCN , the concentration of Cu^+ can be repressed to the point where it is too low to give a precipitate with H_2S . On the other hand, the more highly dissociated $\text{Cd}(\text{CN})_4^{--}$, though giving less Cd^{++} in excess KCN , will give a sufficient concentration of Cd^{++} to allow it to be precipitated with H_2S .

Occasionally, use is made of the inverted form of these functions. For example, if the equilibrium for $\text{Cu}(\text{CN})_3^-$ is written:



the expression for the corresponding equilibrium constant would become:

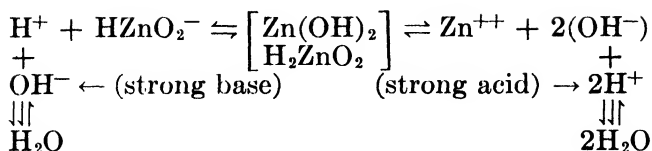
$$\frac{(\text{Cu}(\text{CN})_3^-)}{(\text{Cu}^+)(\text{CN}^-)^3} = K'_{\text{Cu}(\text{CN})_3^-}$$

This constant is called the *stability constant* of the ion. While the dissociation constant is more a direct measure of the concentration of the simple ions in solution, the stability constant is a measure of the concentration of the undissociated complex ions. It will be noted that the stability constant is equal to the reciprocal of the instability constant, *i.e.*,

$$K_{\text{stability}} = \frac{1}{K_{\text{instability}}}$$

Amphoteric Hydroxides. As a rule, slightly soluble metallic hydroxides are soluble in strong acids. Some, however, are soluble in either strong acids or strong bases. Such hydroxides are said to be amphoteric. Aluminum hydroxide, zinc hydroxide, and chromic hydroxide are common examples of amphoteric substances. They are very weak bases and, as will be shown, are also slightly acidic in nature. The dual properties of these substances are expressed by using $\text{Zn}(\text{OH})_2$ as an example. In a saturated solution of $\text{Zn}(\text{OH})_2$, a double equilibrium is set up. The effect of adding hydrogen or hydroxyl ion is shown by the following equation:*

* To visualize better the mechanics of such reactions, one might look upon the zinc hydroxide as being written in the customary form for acids, H_2ZnO_2 , as well as that for a base, $\text{Zn}(\text{OH})_2$.



Addition of either an acid or a base will produce water and result in a neutralization. In the case of the addition of acid, OH^- ions are removed by the formation of water and the equilibrium is shifted to the right, $\text{Zn}(\text{OH})_2$ being dissolved. On adding a base, the H^+ ions are removed by the formation of water and the equilibrium is shifted to the left, $\text{Zn}(\text{OH})_2$ being again dissolved. As can be seen by a little study of the equation, after the $\text{Zn}(\text{OH})_2$ has been dissolved by either a base or an acid, it can be reprecipitated by cautious addition of successive small amounts of an acid or a base.

The fact that not all elements react in this way makes it possible to use this reaction to separate zinc, chromium, and aluminum from iron, manganese, nickel, and cobalt. The hydroxides of these three metals are dissolved in an excess of NaOH and filtered off from the insoluble hydroxides.

It should be apparent from this discussion that there is a definite hydrogen ion concentration at which the solubility of a given amphoteric hydroxide is a minimum. The pH at which an amphoteric substance exhibits its minimum solubility, is known as the *isoelectric point* of that substance.

If, therefore, aluminum hydroxide has been dissolved in excess of either an acid or a base, it may be reprecipitated by changing the hydrogen ion concentration to the value corresponding to the isoelectric point for aluminum hydroxide.

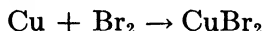
This may be done in either of two ways:

1. An acid or base may be added to increase or decrease the hydrogen ion concentration of the solution until it reaches the proper value; or

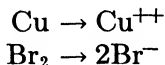
2. In case the aluminum hydroxide was dissolved in excess base, the hydrogen ion concentration can be increased to the proper value by addition of a buffering agent (such as ammonium chloride) to reduce the hydroxyl ion concentration. This method is important to the analytical chemist (see Group III analysis), as the hydrogen ion concentration can be controlled more accurately by use of buffers than by any other readily available means.

Lead, arsenic, antimony, and tin are also readily amphoteric. $\text{Pb}(\text{OH})_2$ dissolves in strong sodium hydroxide solution to form the *plumbite* ion, HPbO_2^- ; arsenous oxide forms *arsenite* ion, $\text{AsO}_3^=$; arsenic oxide forms *arsenate* ion, $\text{AsO}_4^=$; stannous hydroxide, $\text{Sn}(\text{OH})_2$ forms *stannite* ion, HSnO_2^- .*

Oxidation and Reduction. In some reactions, besides the simple reactions between ions, there are changes in the valence of two or more atoms or ions. These reactions, known as *oxidation-reduction* reactions, always involve a transfer of electrons. The simple case of the combination of copper with bromine, when copper is placed in bromine water, illustrates the changes that occur in this type of reaction. Ordinarily the reaction is written thus:



From our knowledge of electrolytes and ionic equations, it should be apparent that a more correct representation of the facts is found in the following:



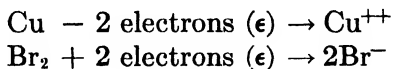
* Tin is peculiar in one respect. In the stannic state, it forms two hydroxides. One, the normal hydroxide (sometimes called *stannic acid*) $\text{H}_2\text{Sn}(\text{OH})_6$, exhibits the normal amphoterism described; the other, *metastannic acid*, is very difficult to dissolve in either acids or bases. This form results when metallic tin is treated with nitric acid. It can be dissolved, however, by converting it to the stannate by an alkaline fusion or by heating with concentrated HCl followed by addition of water. The difference between the reactions of the hydroxides is described as being due to differences in physical state rather than in composition.

No combination of these ions should be indicated since CuBr_2 is highly ionized in solution.

To analyze this further it is necessary for us to recall something of the structure of atoms. It will be remembered (a review of atomic structure as given in any standard inorganic text will help the student) that atoms consist of a centrally located, positively charged nucleus surrounded by orbits in which electrons are traveling. These electrons are present in the exact number required to neutralize the positive charges on the nucleus, so the atom is normally neutral. The outer orbit has the ability to either lose all its electrons or take on more. If it takes on electrons, it will take on just enough to make the total number present in that orbit exactly eight. The question of whether it takes on electrons or loses them depends upon the number already present in that orbit in the neutral atom. If there are less than four, the atom loses electrons; if more than four, it takes on electrons. When either of these processes occurs, the product is an ion.

In the case under consideration, copper has two electrons it can lose. Bromine, having seven electrons in its outer orbit, needs one electron to make up its octet. When copper reacts with bromine, the copper atom gives up its two valence electrons, the copper atom being left with two excess positive charges. The bromine atoms take up the electrons, one to each atom, and thus assume one excess negative charge. Thus, the reaction between copper and bromine solution results in the formation of cupric and bromide ions.

With these facts in mind the above reaction can be correctly written as follows:



The truth of the above representation can be tested by placing a rod of copper in a solution of CuSO_4 , and a

platinum electrode in a solution of KBr containing bromine, connecting the two solutions with a U tube filled with KCl solution and connecting the copper and platinum electrodes to a millivoltmeter (Fig. 10). Although the copper and bromine are not in contact, reaction will occur and a strong current of electricity will flow through the millivoltmeter showing that the reaction is accompanied by a transfer of electrons.

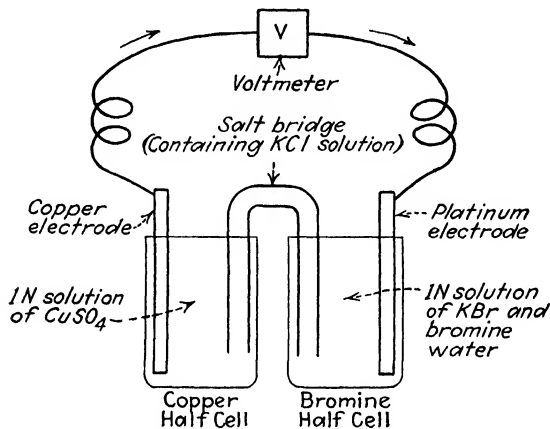


FIG. 10.—Arrangement of a copper-bromine cell.

Elements vary widely as to the readiness with which they tend to lose or gain electrons. Sodium, for example, has a very strong tendency to lose its single outer electron while copper has much less tendency to lose its outer electrons. Chlorine readily takes on one electron while iodine has much less tendency to gain its extra electron. By using these elements in cells like that described above it has been possible to measure these relative tendencies in terms of volts. The element is placed in a solution 1*N* with respect to its ions. This half-cell* is connected to a hydrogen

* An electrode immersed in a solution of its ions is known as a *half-cell*. Two half-cells connected by a salt bridge (a U tube filled with a solution of some salt such as KCl) constitute a cell.

electrode, by means of the salt bridge (U tube) described, and the voltage of the resulting combination is measured. The hydrogen electrode is used as a reference base, and, consequently, the voltage measured is assigned to the element being used. Tables of these *normal electrode potentials* are very useful in predicting the probable completeness of given oxidation-reduction reactions. A few of these potentials are given in Table I (see Appendix).

The neutral atoms of those elements at the top of this list have the strongest tendency to *lose* electrons, and their ions have the least tendency to take on electrons again and become neutral atoms. Those at the bottom have the strongest tendency to *gain* electrons, their ions having the least tendency to lose electrons. The voltage of any combination (which is a measure of the tendency for reaction to occur) is found by taking the algebraic difference of the individual electrode potentials of the components. For example, it may be necessary to determine the voltage of a cell made up of a normal zinc electrode and a normal chlorine electrode.

$$\text{Zn} = +0.76$$

$$\text{Cl} = -1.36$$

Therefore the voltage of this cell will be

$$0.76 - (-1.36) = 0.76 + 1.36 = 2.12 \text{ volts}$$

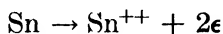
Where the resulting voltage is as high as this, the reaction will be complete, *i.e.*, zinc and chlorine will react with great vigor.

Electrode potentials have a very important application to some phases of analytical chemistry. For example, it is necessary to reduce tin from the stannic to the stannous state before testing for this metal. To do this it is necessary that some substance be chosen as reducing agent that

has a more *negative* oxidation-reduction potential than the potential for the reaction



If the latter is looked up in a table of oxidation-reduction potentials, it is found that the potential for this reaction is +0.13 volt. This means that any metal having an electrode potential more negative than +0.13 volt will reduce stannic ion to stannous ion. The greater the difference between the two (*i.e.*, the greater the potential of the cell made up of a combination of the two), the more complete and rapid will be the reduction of the stannic ion. However, the reaction

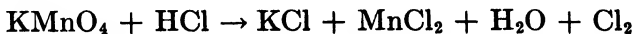


has a potential of -0.13 volt. Any metal more negative than this will reduce the stannic ion completely to the metallic state. Consequently, a metal whose electrode potential is between +0.13 volt and -0.13 volt is necessary to bring about the desired reduction without at the same time reducing Sn^{++} to Sn^0 . Lead (-0.12 volt) is one such metal and is sometimes used for this reduction. However, it reacts so slowly that more active metals (*e.g.*, zinc, aluminum, or magnesium) are usually used, any metallic tin being redissolved in hydrochloric acid.

Balancing Oxidation-reduction Equations. Balancing oxidation-reduction equations by the trial-and-error method is usually difficult owing to the complexity of the reaction. The above discussion, however, opens other methods to us, the principle of which consists of the balancing of the number of electrons involved.

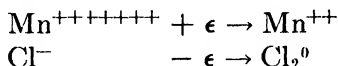
These methods are as follows:

I. *Valence-electron Method.* Five steps are needed in this method. To illustrate, let us consider the following equation:

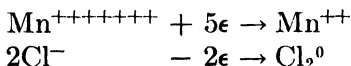


The steps are as follows:

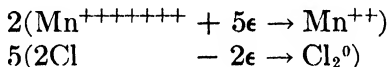
1. Pick out the elements that undergo changes in valence and write these changes, with their electron changes, as equations. In the above equation, Mn^{++++++} changes to Mn^{++} and some of the Cl^- changes to Cl_2^0 .



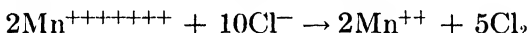
2. Balance the atoms and the electrons in each equation.



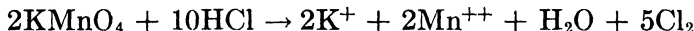
3. Multiply each of these equations throughout by a number which will make the number of electrons in each equal to that in the other.



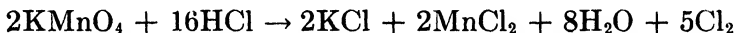
4. Add all those atoms on the left side of the equations and place them on the left side of a new equation; do similarly for those on the right side.



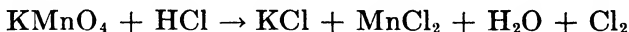
5. Using these numbers in the original equation balance the atoms and molecules as far as possible.



Ten Cl^- call for ten HCl molecules. However, there are eight oxygen atoms in the two KMnO_4 molecules which form eight molecules of water—requiring sixteen hydrogen ions. Since HCl is the only source of H^+ , at least sixteen HCl molecules are required. The chloride ion from the six extra HCl molecules react with the K^+ and Mn^{++} and the equation is thus completely balanced.

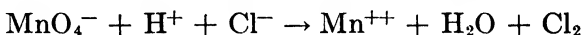


II. *Ion-electron Method.* There are six steps to this method of balancing oxidation-reduction equations. Using the same equation as before to make comparison easy:



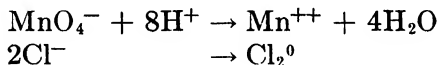
the steps are as follows:

1. Write the equation in terms of the ions present and cancel all those ions that go through unchanged:



The H^+ must be retained on the left as it goes to form the slightly dissociated water. The Cl^- are retained on the left—though canceled on the right—because some of them go into the form of Cl_2 molecules.

2. Write two equations, one for each *ion* that undergoes an *electronic* change and balance the atoms and ions in each.



3. Take the *algebraic* sum of the charges on the right side of each equation and *subtract algebraically* from the algebraic sum of the charges on the left. The difference will give the number of electrons to add (algebraically) to the left side of the equation to make it balance electrically.

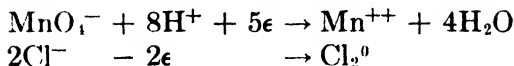
Thus, for the first equation,

$$(-1 + 8) - (+2 + 0) = 5$$

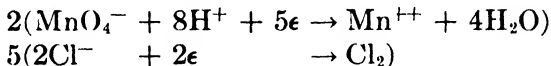
which means that five electrons must be added to the left side of this equation. For the second equation,

$$(-2) - (0) = -2$$

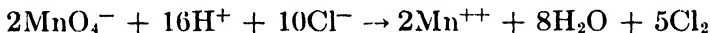
which means that two electrons must be subtracted from the left side of this equation. Therefore, to balance these completely.



4. Multiply each of these equations throughout by a number which will make the number of electrons in each equal to those in the other.



5. Add all those ions on the left side of the equations and place them on the left side of a new equation; do similarly for those on the right side. This will give a completed *ionic* equation for the reaction.



6. Complete the equation by writing the proper coefficients in the original equation using the same method as described for the valence-electron method in part 5.

In general, either of these two methods is applicable to any oxidation-reduction equation. Strictly speaking, however, the latter method is preferable for reactions in solution where the reaction is actually between ions.

MATHEMATICAL RELATIONSHIPS

In previous paragraphs there has been given a qualitative discussion of various laws. For practical use it is usually important to be able to consider the mathematical aspects of a given analytical problem. Ionization constants and solubility products mean little to one who does not know how to use them or how they were derived. For this reason it is important to practice working such problems until the necessary understanding is reached.

From the standpoint of the student, the more important types of problems are the following:

1. *Weak electrolytes:* These involve the calculation of the concentration of one ion of a weak electrolyte when—

a. The ionization constant and the concentration of the weak electrolyte are known.

b. The ionization constant, the concentration of the weak electrolyte, and the concentration of a second ion are known (the case of buffer solutions).

c. The ionization constant of the weak electrolyte and the concentration of all electrolytes present are known. An example of this case is the adding of a strong electrolyte to a buffer solution.

2. *Solubility product:* These involve

a. The calculation of the concentration of one ion of a slightly soluble salt (in a solution saturated with respect to its ions) when the concentration of the other ion and the solubility product constant of the salt are known.

b. The calculation of the solubility product constant from the solubility of the substance.

c. The calculation of the solubility of a slightly soluble salt from its solubility product constant.

d. The calculation, from solubility product constants, of the efficiency of separation of two given ions which are being precipitated by a common reagent.

In the case of each of these problems, it is only necessary to choose the appropriate formula* and substitute the given values in it. An example of each type should serve to illustrate the method to be used.

Problems Involving Weak Electrolytes. *Type 1 a.* The first type of problem always makes use of the equation for the ionization constant of the weak electrolyte. For example, the hydroxyl ion concentration in a 0.01*M* solution of NH_4OH is found by first deriving the equation for the equilibrium constant of NH_4OH , then substituting the

* It is best to learn how to derive the various formulas rather than to depend upon the memory. The derivations are simple and are much less likely to lead to the use of the wrong formula.

proper numerical values in it. The ionization that occurs is



Therefore, applying the law of mass action, the equation is found to be $[(\text{NH}_4^+)(\text{OH}^-)]/(\text{NH}_4\text{OH}) = K_b$. K_b for NH_4OH is 1.8×10^{-5} ; and recalling from earlier discussions that (NH_4^+) , (OH^-) , and (NH_4OH) mean the *mol concentrations* of NH_4^+ , OH^- , and NH_4OH molecules, respectively, substitutions can be made and the hydroxyl ion concentration calculated. To do this, however, two things must be remembered. First, OH^- and NH_4^+ must be present in equal concentrations—each molecule that has ionized to give an OH^- has, at the same time, given an NH_4^+ . Therefore, if we let X equal the OH^- concentration (which is what we are trying to calculate), it must also equal the ammonium ion concentration. Therefore X can be substituted for each of these in the above equation.

The second point to remember is that, in the case of any weak electrolyte, only a very small fraction of the molecules present are in the ionized state at any given time. Consequently, it is possible, without introducing any serious error for ordinary purposes, to assume that the concentration of NH_4OH molecules is equal to the original concentration placed in the solution, *i.e.*, (in this case) $0.01M$.

Thus, using these simplifications, it is found that

$$\frac{(X)(X)}{0.01} = 1.8 \times 10^{-5}$$

$$X^2 = 1.8 \times 10^{-5} \times 0.01 = 1.8 \times 10^{-7}$$

$$X^2 = 18 \times 10^{-8}$$

$$X = \sqrt{18} \times 10^{-4} \text{ mol per liter} = \text{OH}^- \text{ concentration}^*$$

* To calculate the *hydrogen ion* concentration of a solution of ammonium hydroxide, it is first necessary to calculate the hydroxyl ion concentration as described here. Then the concentration found for the OH^- is substituted in the equation

$$(\text{H}^+)(\text{OH}^-) = K_w$$

and the hydrogen ion concentration is calculated (see Water and pH Values).

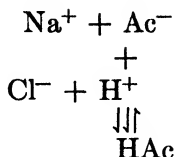
Type 1 b. These problems refer to solutions of a mixture of a weak electrolyte with a salt having a similar ion. For example, calculate the hydrogen ion concentration in a solution $0.01M$ with HAc and $0.1M$ with NaAc. Again the formula for the ionization constant of the weak electrolyte (HAc) is used.

$$\frac{(\text{H}^+)(\text{Ac}^-)}{(\text{HAc})} = K_a$$

The concentration of HAc molecules is assumed to be that of the original acetic acid. NaAc, however, is a strong electrolyte (as are practically all salts) and may be assumed to ionize completely giving a solution $0.1M$ with respect to each of the ions, Na^+ and Ac^- . A small amount of Ac^- comes from the ionization of the HAc, but this is so small compared to the quantity coming from the NaAc that it can be ignored. Therefore, if it is assumed that all the Ac^- comes from the NaAc, its concentration may be taken as $0.1M$. K_a for HAc is 1.86×10^{-5} . Using these values as in the above equation,

$$\begin{aligned}\frac{(\text{H}^+)(0.1)}{0.01} &= 1.8 \times 10^{-5} \\ (\text{H}^+)(0.1) &= 1.86 \times 10^{-5} \times 0.01 = 1.86 \times 10^{-7} \\ \text{H}^+ &= \frac{1.86 \times 10^{-7}}{0.1} = 1.86 \times 10^{-6} \text{ mol per liter}\end{aligned}$$

Type 1 c. In the case of a mixture of a low concentration of a strong acid and a *higher* concentration of the salt of a weak acid, another factor enters. It is found that in such mixtures the strong acid reacts quantitatively with the salt forming a mixture of the weak acid and the salt of the strong acid. For example, if HCl is added to NaAc the following reaction occurs:



If the salt is in excess, the result will be a mixture of Na^+ (from the NaCl and the excess NaAc), Ac^- (chiefly from the excess NaAc), Cl^- (from the NaCl), H^+ (from the ionization of the HAc formed), and HAc molecules. The only weak electrolyte present is HAc ; therefore use is again made of the equation for its ionization constant, in calculations. To take a typical example, calculate the hydrogen ion concentration in a solution $0.1M$ with NaAc and $0.01M$ with HCl . When the solution was first prepared, the above reaction occurred, forming approximately 0.01 mol of HAc and, consequently, *removing* 0.01 mol of NaAc . This leaves $0.1 - 0.01$, or 0.09 mol per liter, of NaAc . This ionizes, giving 0.09 mol of Ac^- . Therefore, the solution is now $0.01M$ with HAc and $0.09M$ with Ac^- . Therefore substituting in the equation,

$$\frac{(\text{H}^+)(\text{Ac}^-)}{(\text{HAc})} = K_a$$

it is found that

$$\begin{aligned}
 \frac{(\text{H}^+)(0.09)}{0.01} &= 1.8 \times 10^{-5} \\
 (\text{H}^+)(0.09) &= 1.8 \times 10^{-7} \\
 \text{H}^+ &= \frac{1.8 \times 10^{-7}}{9 \times 10^{-2}} = 0.2 \times 10^{-5} \text{ mol per liter}^*
 \end{aligned}$$

* The solution is identical with a solution prepared by adding sufficient NaCl , NaAc , and HAc to water to make a solution $0.01M$ with NaCl , $0.09M$ with NaAc , and $0.01M$ with HAc . The presence of the NaCl may be disregarded here, though, as will be learned later, it has a small effect on the *apparent* concentration of the other ions (see Salt Effect). For this

In a similar manner it is possible to calculate the concentration of OH^- ions in solutions of weak bases containing a salt of a weak base (Type 1b) or in solutions containing a mixture of a strong base and a greater concentration of a salt of a weak base (Type 1c). In such cases the formula for the ionization constant of the weak base is used. For example, if NH_4OH or its salts are involved in these problems, the equation is as follows:

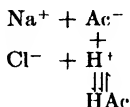
$$\frac{(\text{NH}_4^+)(\text{OH}^-)}{(\text{NH}_4\text{OH})} = K_b$$

The reasoning and substitutions are similar to those in the cases described above.

Problems Involving Solubility Products. These are very similar in nature to those for weak electrolytes. Again it is a question of choosing the proper equation (which is, this time, the equation for the solubility product constant of the

reason, it is legitimate to treat the problem as dealing with a solution of HAc and NaAc in pure water.

In case the concentration of the strong acid is greater than the concentration of the salt of the weak electrolyte, the problem is resolved into one of calculating the concentration of H^+ from the unreacted strong acid. For example, if a solution is made $0.1M$ with HCl and $0.01M$ with NaAc, a reaction again occurs:



This time, the acetate ion concentration is lower than the hydrogen ion concentration. Consequently, reaction will occur until practically all the Ac^- is used. This will leave a solution which is equivalent to a mixture of NaCl, HCl, and HAc. The HCl, being a strong electrolyte, furnishes so much more H^+ than does the HAc that the latter can be regarded as yielding no H^+ at all. Hence, it is only necessary to calculate the concentration of H^+ coming from the HCl. Using reasoning similar to that above, it will be found that the solution is $0.09M$ with HCl. Therefore the hydrogen ion concentration, assuming complete ionization of the HCl, is 0.09 mol per liter.

slightly soluble substance involved) and substituting in it the *known* values.

Type 2 a. Assume that it is desired to calculate the maximum concentration of Ag^+ that can remain in a solution in equilibrium with $0.001M$ I^- ion. Obviously, the slightly soluble substance involved is AgI (whose $K_{s,p}$ is 1.5×10^{-16}). The equation for the solubility product constant is

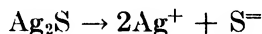
$$(\text{Ag}^+)(\text{I}^-) = K_{s,p}$$

Substituting in this,

$$\begin{aligned} (\text{Ag}^+)(0.001) &= 1.5 \times 10^{-16} \\ \text{Ag}^+ &= 1.5 \times \frac{10^{-16}}{0.001} = 1.5 \times \frac{10^{-16}}{10^{-3}} = 1.5 \times 10^{-13} \text{ mol per liter} \end{aligned}$$

Type 2 b. This type of problem involves the calculation of the solubility product constant of a slightly soluble salt from its solubility. For example, given that the solubility of Ag_2S is approximately 1.35×10^{-17} mol per liter, calculate the $K_{s,p}$ for Ag_2S . To do this it is necessary to know and remember one other point.

When one molecule of Ag_2S ionizes, it gives two Ag^+ and one $\text{S}^{=}$.



Consequently, since a saturated solution of Ag_2S contains 1.35×10^{-17} mol of the latter, *completely ionized*, it must contain *two times* that much, or 2.7×10^{-17} mol per liter of Ag^+ , and one times that much, or 1.35×10^{-17} mol per liter, of $\text{S}^{=}$. Reviewing the solubility product principle gives

$$(\text{Ag}^+)^2(\text{S}^{=}) = K_{s,p}$$

as the equation involved. Substituting in this

$$\begin{aligned} (2.7 \times 10^{-17})^2(1.35 \times 10^{-17}) &= K_{s,p} \\ (7.29 \times 10^{-34})(1.35 \times 10^{-17}) &= K_{s,p} \\ K_{s,p} &= 9.84 \times 10^{-51} = 0.984 \times 10^{-50} \end{aligned}$$

If the concentration had been given in *grams* per liter, the first step would have been to convert it to mols per liter. This is done by dividing the number of grams in 1 liter by the molecular weight of the salt.

Type 2 c. The reverse of the problems of Type 2b would be to calculate the solubility of a slightly soluble substance from the solubility product constant. For example, given that K_{sp} for Ag_2CrO_4 is 3.3×10^{-12} , calculate the solubility of Ag_2CrO_4 . Again it must be remembered that when 1 mol of Ag_2CrO_4 ionizes it gives 2 mols of Ag^+ and 1 mol of $\text{CrO}_4^{=}$. If S represents the solubility of Ag_2CrO_4 in mols per liter, the concentration of Ag^+ in the saturated solution will be $2S$ and that of $\text{CrO}_4^{=}$ will be S . Again, using the solubility product constant equation,

$$(\text{Ag}^+)^2(\text{CrO}_4^{=}) = K_{sp}$$

We can substitute and calculate as follows:

$$(2S)^2(S) = 3.3 \times 10^{-12}$$

$$(4S^2)(S) = 3.3 \times 10^{-12}$$

$$4S^3 = 3.3 \times 10^{-12}$$

$$S^3 = \frac{3.3}{4} \times 10^{-12} = 0.82 \times 10^{-12}$$

$$S = \sqrt[3]{0.8 \times 10^{-12}} = 0.94 \times 10^{-4} \text{ mol per liter} \\ = \text{solubility of } \text{Ag}_2\text{CrO}_4$$

To get the solubility of Ag_2CrO_4 in *grams* per liter, it is only necessary to multiply the above answer by the molecular weight of Ag_2CrO_4 .

Type 2 d. This type of problem involves the calculation of the ratio of the concentrations of two slightly soluble substances *having a common ion*, in a solution saturated with respect to each. For example, assume that a solution is $0.1M$ with respect to each of the ions, Pb^{++} and Mn^{++} . If H_2S is passed into the solution, PbS will precipitate. This removes Pb^{++} from the solution (leaving all the Mn^{++} in solution). After a time, however, the concentration of

the Pb^{++} will be so reduced that the sulfide ion concentration, which, in accordance with the solubility product principle, has been increasing as the lead ion concentration decreased, reaches a value sufficiently high for the precipitation of MnS . It is desired, therefore, to calculate what will be the concentration of Pb^{++} left in solution at the moment MnS first begins to precipitate. This is a measure of the efficiency of the separation of Pb^{++} and Mn^{++} by the use of H_2S .

It is evident that the sulfide ions present in the solution at that moment are responsible for the precipitation of both PbS and MnS . Consequently, write the equations for the solubility relationship of each

$$\begin{aligned}(\text{Mn}^{++})(\text{S}^{=}) &= K_{s.p. \text{ MnS}} \\ (\text{Pb}^{++})(\text{S}^{=}) &= K_{s.p. \text{ PbS}}\end{aligned}$$

then divide the upper equation by the lower equation

$$\frac{(\text{Mn}^{++})(\text{S}^{=})}{(\text{Pb}^{++})(\text{S}^{=})} = \frac{K_{s.p. \text{ MnS}}}{K_{s.p. \text{ PbS}}}$$

and cancel the sulfide ion concentrations. This may be done, for, since all three ions are present in the same solution, the sulfide ion concentration is the same for both reactions.

The resulting equation will be

$$\frac{(\text{Mn}^{++})}{(\text{Pb}^{++})} = \frac{K_{s.p. \text{ MnS}}}{K_{s.p. \text{ PbS}}}$$

Now the given values may be substituted in this equation ($K_{s.p. \text{ PbS}} = 10^{-28}$, $K_{s.p. \text{ MnS}} = 10^{-15}$) and the concentration of Pb^{++} calculated (at the moment MnS first begins to precipitate, the concentration of Mn^{++} will be $0.1M$):

$$\frac{0.1}{(\text{Pb}^{++})} = \frac{10^{-15}}{10^{-28}} = \frac{1}{10^{-13}}$$

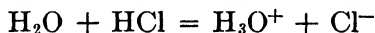
$$(\text{Pb}^{++}) = (10^{-13}) \times (0.1) = 10^{-14} \text{ mol per liter}$$

This shows that the separation is very complete.

More complicated problems than these may be met, but it will be found that they are merely combinations or variations of those considered above.*

MODERN THEORIES OF ELECTROLYTES

Hydronium Ion. In the treatment of solutions, it has been the belief, until recent years, that acids give hydrogen ions when placed in solution. Ionization of acids was presumed to be the simple dissociation of the acid molecule into positively charged hydrogen ions and negatively charged ions. A study of the properties of electrolytes in nonaqueous solvents shows that ionization is not so simple as this, however, revealing many phenomena that are not explained by the earlier theory. After many experimental data had been studied, Bronsted and others finally arrived at the conclusion that there is a definite reaction between the acid molecule and the molecule of the solvent, resulting in the union of the H^+ ions and the solvent to form *solvated* ions.† For example, the ionization of hydrogen chloride in water would be represented by the equation



the H_3O^+ being called the *hydronium* ion.

* In the Appendix will be found a list of problems of the various types considered in this and earlier sections. Most of these have practical applications to the analytical procedure. Consequently, the student should work them and try to see the application at the same time.

† There is evidence for the belief that *all* ions in solution, both negative and positive, are solvated. Conductivity measurements on solutions give values lower than those calculated on the basis of the mass and charge of the ions involved, the deviation being explained, in part, by the theory that solvent molecules attach themselves to the ions and act as a "drag" on the movements of the ions. As a rule, however, the other hydrated ions are much less stable than is the hydronium ion, H_3O^+ , formed when acids dissolve in *water*.

An excellent discussion of the solvation of ions is given in the section on complex ions in "Qualitative Analysis and Chemical Equilibrium" by Hogness and Johnson, Henry Holt & Company, New York, 1937.

This theory has almost completely supplanted the earlier conception of ionization. The chief reasons for the widespread acceptance of the newer theory are as follows:

1. Recent investigations of electrolytes in nonaqueous solvents having different dielectric constants* have shown that if ionization were due to the dielectric effect of the solvent alone (as was formerly believed) it would require a solvent of much higher dielectric constant than any substance known.

2. It has been found that such substances as hydrogen chloride (which is nonpolar† in the solid, liquid or gaseous state) are electrolytes only when dissolved in certain solvents. The molecules of these solvents are all characterized by containing an atom or atoms having one or more unshared electron pairs which are capable of holding protons (or H^+) and forming fairly stable complex ions in this manner. For example, in benzene, C_6H_6 ; ethyl bromide, C_2H_5Br ; toluene, C_7H_8 ; and similar solvents, hydrogen chloride exhibits none of the properties of an acid and does not conduct electricity. No evidence of ionization has been found. On the other hand, solutions of hydrogen

* It has long been known that if two oppositely charged bodies were placed near each other they exerted a force of attraction upon each other. The magnitude of the force, however, depends, among other things, upon the nature of the medium between the two bodies. Those substances that diminish the force to the greatest extent, are said to have high *dielectric constants*. Thus, the dielectric constant of a given substance is a measure of its ability to weaken the force of attraction between charged bodies, if placed between them.

The basis for the theory that solvents of high dielectric constant should be the best ionizing solvents should be self-evident when it is recalled that ions are charged bodies.

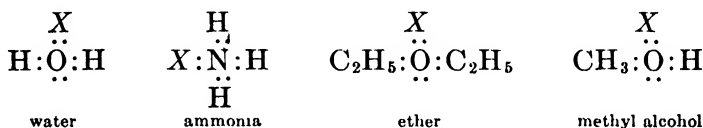
† There are two meanings that may be applied to the term *polar molecule*. In one case, the term applies to molecules in which the atoms are so arranged that one side of the molecule has a surplus of positive charges while the other side has a surplus of negative charges. In the second case, the term applies to molecules having ionic valences.

The term *nonpolar* as used here refers to molecules in which all valences are of the shared-electron-pair type.

chloride in water, ether, liquid ammonia, methyl alcohol, etc., are excellent conductors of electricity and give many other evidences of containing a highly ionized solute.

The Raman spectra and the infrared absorption spectra of these solutions show no evidence of hydrogen chloride molecules whereas solutions of hydrogen chloride in ethyl bromide and other such solvents give distinct spectra of the molecules of solute (42).

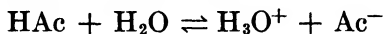
Molecules of water, ammonia, ether, and methyl alcohol have the following electronic arrangements to which has been attributed their ionizing effect. The position taken by the proton is marked by X .



3. To ionize gaseous hydrogen chloride in a discharge tube requires a large amount of energy. Presumably, the ionization of hydrogen chloride in solution would require the same quantity of energy, and the only possible source of so much energy is that set free by some reaction in the solution such as that postulated by the new theory.

There are many more reasons for accepting the theory of solvated ions. However, this is sufficient to give some idea of the reasons for the wide acceptance of this conception of ionization.

In the light of this discussion, it is necessary that the mathematical relationships formulated earlier be revised slightly. Thus, the ionization of the weak electrolyte, acetic acid, should be represented as



The equilibrium expression, therefore, should be written

$$\frac{(H_3O^+) \times (Ac^-)}{(HAc) \times (H_2O)} = K$$

However, the concentration of the water molecules may be considered as varying so little in different solutions as to remain constant. Consequently, the above expression can be changed (as was done for the equilibrium expression treating water as a weak electrolyte) to the following:

$$\frac{(\text{H}_3\text{O}^+) \times (\text{Ac}^-)}{(\text{HAc})} = K_a$$

It has been shown experimentally that all the hydrogen ion present is in the form of hydronium ion. Since the term H_3O^+ is expressed in mols, the numerical value will be the same as if expressed as H^+ . Consequently, the value for K_a will be the same as that previously given, *i.e.*, 1.86×10^{-5} .

By similar reasoning, the expression for the ion product of water is shown to be

$$(\text{H}_3\text{O}^+) \times (\text{OH}^-) = K_w$$

and the pH of a solution can be calculated by changing the expression for this factor to

$$\text{pH} = \log \frac{1}{(\text{H}_3\text{O}^+)}$$

Salt Effect; the Debye-Hückel Theory (44). It has been pointed out that the solubility product relationship does not hold strictly true when the total ion concentration of the solution is high. If, to a solution saturated with a slightly soluble salt, a highly soluble salt is added, the solubility of the slightly soluble salt increases as the concentration of the more soluble salt is increased. For example, it was found by Bray and Winninghoff (43) that thallous chloride, TlCl , has a solubility of about 0.016 mol per liter in pure water while in 0.1M KNO_3 solution, which has no ions in common with those from TlCl , it has a solubility of 0.019 mol per liter.

This phenomenon, known as the salt effect, seems more pronounced with some salts than with others, the difference depending little on the ions added, but much more on the valence types to which they belong. For example, a salt consisting of two bivalent ions (*e.g.*, MgSO_4) has a much greater salt effect than does an equivalent concentration of a uni-univalent salt such as KNO_3 ; a salt consisting of two trivalent ions has more effect than the bi-bivalent type; and so forth.

A similar phenomenon is noted with weak electrolytes. It has been found that in strong solutions of weak electrolytes or solutions of weak electrolytes containing a high concentration of any salt, the ionization constant has a greater numerical value than normal.

Even strong electrolytes are influenced by the salt effect. Conductivity measurements on solutions of NaCl and other strong electrolytes show an increase with dilution; but, instead of the conductivity gradually increasing with dilution as in the case of weak electrolytes, with strong electrolytes it quickly reaches a maximum. This was formerly thought to be due to an increase in the degree of ionization, as in the case of weak electrolytes. This explanation, however, left much to be desired, for it supplied no explanation for the apparently great increase in ionization of strong electrolytes with dilution as compared to the more gradual increase exhibited by weak electrolytes. Work on such solutions finally led to the formulation of the Debye-Hückel theory, the essential points of which are as follows:

1. Strong electrolytes (such as NaCl and KCl) are completely ionized even in strong solutions. This idea is borne out by the fact that X-ray examination of the crystals of these two salts shows them to be ionized even in the solid state. There is no justifiable reason, therefore, for believing that when these substances are placed in solution the

ions forsake their greater freedom for an existence as molecules.

2. Each ion is surrounded by a "sphere of influence" (due to its electrical charge) which will tend to act on any ion of opposite charge passing through that region.

3. The size and strength of the sphere of influence of bivalent ions are greater than those of monovalent ions, and so forth.

4. As a given ion moves through the solution, it passes through the fields of attraction of many other oppositely charged ions with the result that there is a mutual "dragging" effect which slows the movement of the ions and reduces their activity. This effect is greatest in concentrated solutions, diminishing to a negligible effect in very dilute solutions.

According to this theory, therefore, the ions are restrained in their movements in concentrated solutions. This makes them act as if their concentration were lower than it really is.* With these facts in mind, Debye and Hückel, and Bronsted and La Mer were able, for many solutions, to calculate an *effective concentration* or *activity* which, substituted in the ordinary equilibrium expressions, enabled them to calculate ionization constants that held true over a much wider range of concentrations than was formerly possible.†

* It should be obvious, now, why the solubility product relationship does not apply, with any mathematical accuracy, to saturated solutions of more soluble salts. For example, at 20°C. a saturated solution of NaCl contains approximately 6.2 mols of solute per liter. If complete ionization is assumed, such solutions contain 6.2 mols per liter of each, Na^+ and Cl^- . At much lower ion concentrations than this, the salt effect is very strong. Consequently, the usual calculations will be thrown off in such solutions.

† The original formulas by which activities were calculated are too complicated for presentation here. A simplified formula, however, developed by Bronsted and La Mer (62), is

$$-\ln f = 0.5z_1z_2\sqrt{\mu}$$

where f is the *activity coefficient*, z_1 , and z_2 are the number of charges on the anion and cation, respectively, and μ is the *ionic strength* of the solution. The latter is a measure of the "drag" exerted (*Continued on opposite page*)

Coprecipitation Phenomena. Imperfect reports are by no means uncommon for students in qualitative analysis, but knowledge of some of the *causes* of such mistakes will help reduce them to a minimum. There are many such causes (most of which will be found in the notes on the laboratory procedure) but some of the greatest errors are due to the phenomena classified collectively under the term *coprecipitation*.

1. *Inclusion.* Certain gelatinous precipitates, such as aluminum and ferric hydroxides, consist of extremely tiny crystals intermeshed in such a fashion as to form minute pockets in which are enclosed small portions of the original solution. Washing does not remove these protected portions of solution; and when the precipitate is redissolved, the resulting solution will be contaminated with ions that should have remained in the original filtrate. In the analytical procedure used in some texts, ferric, chromic, and aluminum hydroxides are formed from hydroxyl ions furnished by the hydrolysis of ammonium benzoate. This method (recommended by Kolthoff) results in a less gelatinous, more crystalline precipitate and reduces the error due to inclusion.

2. *Adsorption.* Certain precipitates (especially the gelatinous hydroxides and certain metallic sulfides) have large exposed surfaces which are capable of adsorbing other ions

by the ions upon each other. For simple salts μ can be calculated from the formula

$$\mu = \frac{C_1 z_1^2 + C_2 z_2^2}{2}$$

where C_1 and C_2 are the concentrations of the anions and cations respectively, and the other terms have the meanings given above. The relationship between the actual concentration of an ion C and its activity a is given by the expression

$$a = f \times C$$

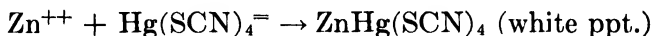
By using the activity instead of true concentrations, calculations involving solutions of weak electrolytes or slightly soluble substances will be accurate over a much wider range of concentrations.

in large quantities. This surface phenomenon is not thoroughly understood, being due, probably, either to a surface reaction or to a preponderance of one type of valence over another which enables the ions on the crystal face to attract ions of opposite charge and hold them to its surface. Thus, ions which would otherwise remain in solution are carried down with the precipitate, often in such concentrations as to give misleading results.

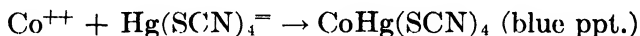
3. *Mixed-crystal Formation.* Most of the trouble caused by coprecipitation is due to the formation of mixed crystals of isomorphous compounds. *Isomorphous compounds* are those having the same type of crystalline structure and atoms of nearly the same size. Cadmium sulfide and barium sulfide are isomorphous, as are also sodium chloride and potassium chloride. When cadmium sulfide is precipitated in Group II, some barium ions occasionally attach themselves, momentarily, to the sulfide ions on the surface of the cadmium sulfide. Many of these barium ions escape into the solution again, but some of them fail to escape before more cadmium and sulfide ions attach themselves to the surface of the solid and enclose the barium ions, preventing their going back into the solution. This results not only in contaminating the precipitate with barium ion but also, in extreme cases where the cadmium ion concentration is much higher than that of the barium ion, in removing so much barium ion that the test for the latter in Group IV is missed entirely. In case the cadmium ion concentration is extremely high, therefore, it is often necessary to redissolve the Group II precipitate in as small a volume of acid as possible and reprecipitate with hydrogen sulfide. In this more concentrated solution, some of the barium ion will escape coprecipitation and the two filtrates, combined and concentrated by evaporation, may be used for the barium test.

Occasionally, however, coprecipitation can be of service to the analyst. For example, the tests for zinc, copper and

cobalt, using ammonium mercuric thiocyanate reagent, depends, for their greatest sensitivity, on the formation of mixed crystals. The test is made for cobalt or copper by adding zinc ion to the solution and then adding the reagent. In the absence of cobalt or copper the following reaction occurs;



If cobalt is present, the following additional reaction occurs:



If both ions are present, mixed crystals of these two compounds will form, the precipitate having a blue color, the depth of which will be greater, the larger the concentration of cobalt ion. It is found that, carried out in this way, it is possible to detect cobalt in solutions that would give no precipitate whatsoever with the reagent in the absence of zinc.

In the case of the copper and zinc tests, the same type of reaction is involved. However, if the copper is present in concentrations greater than the zinc, an apple-green precipitate of copper mercuric thiocyanate will form.

ORGANIC COMPOUNDS IN ANALYSIS

Organic Reagents.* It has been found that many organic compounds give tests for metallic ions that are more specific and sensitive than those given by any known inorganic reagent. The reactions involved are often quite complicated and difficult for one not studied in organic chemistry to comprehend. Occasionally the reaction is of the ordinary double decomposition type, but more often it involves coordinate linkages in addition to the ordinary type.

* *Note to teacher:* It is not intended that students who have had no organic chemistry should attempt the study of this section. This material is included only for those sufficiently advanced in chemistry.

With few exceptions organic analytical reagents may be divided into two groups:

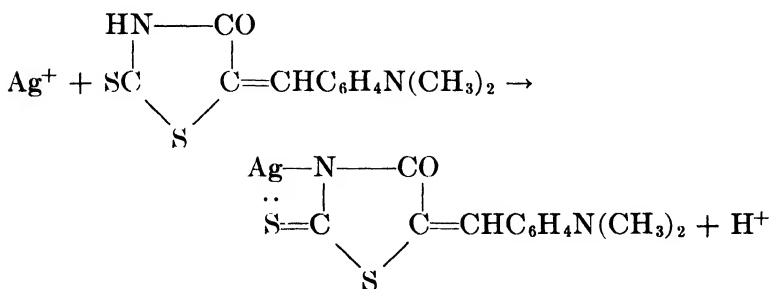
1. Those reacting only through coordinate valences.
 2. Those having one or more acidic groups, or an acidic group and an atom having an unshared pair of electrons.
- The acidic groups that are the most important are:

- a. The oxime, or $=\text{NOH}$ group ($=\text{NOH} \rightleftharpoons =\text{NO}^- + \text{H}^+$)
- b. The hydroxyl, or $-\text{OH}$ group
- c. The mercaptan, or $=\text{SH}$ group
- d. The imino, or $=\text{NH}$ group ($=\text{NH} \rightleftharpoons =\text{N}^- + \text{H}^+$)
- e. The carboxyl, or $-\text{COOH}$ group
- f. The amido, or $=\text{CONH}_2$ group
- g. The sulfonic, or $-\text{SO}_3\text{H}$ group

These are all important in analytical work, with the exception of the carboxyl and sulfonic groups.

Of the many organic reagents, only four of the most common will be discussed here.

Rhodanine, 5-(*p*-dimethylaminobenzal) rhodanine, is one of the reagents used for the identification of mercury, silver, etc. The reaction with silver may be written as follows (45, 46):



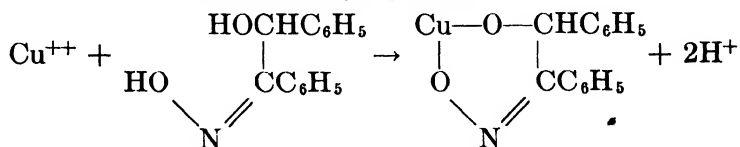
It will be noted that this is the case of an imido group reacting in the normal fashion, together with the formation of a four-membered ring one part of which is a coordinate linkage between the metal and the sulfur. The formation

of coordinate bonds with reagents is much simplified by considering that the metallic ions, in such cases, are really forming complex ions of much the same type considered earlier. It will be recalled that molecules which readily form complex ions always have one or more atoms upon which there are unshared electron-pairs.

Organic reagents that depend upon the use of coordinate linkages always have one or more atoms of this type. Consequently, the reaction of a reagent such as 5-(*p*-dimethylaminobenzal) rhodanine is partly a normal double decomposition reaction and partly a type of complex ion formation.

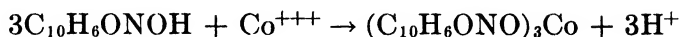
It will be found that the reaction of Ni^{++} with dimethylglyoxime is of this same type. In compounds where such rings are possible, it will be found that, in accordance with the Baeyer Strain Theory, if two rings are possible, that one which comes closer to giving a six-membered ring will be the most probable—and the most stable, if formed. Five- and six-membered rings are the most stable of all, while three-membered rings are almost unknown. The atoms which may make up the ring are carbon, oxygen, nitrogen, sulfur, and the metallic atom. Coordinate linkages, of the type shown above, connect the metallic atom to either a sulfur, a nitrogen, or an oxygen atom—seldom, if ever, to the carbon—as these three atoms each have one or more pairs of unshared electrons.

α -Benzoin-oxime (cupron) is usually used for copper. The reaction involved is one of simple double decomposition as is shown in the following equation:



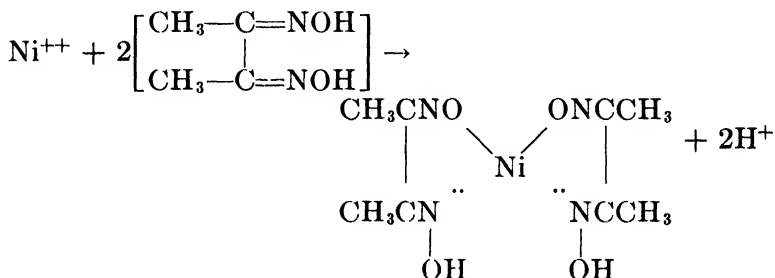
α -Nitroso- β -naphthol is used for cobalt. It is an excellent reagent, as nickel, unless in unusually large con-

centrations, does not interfere. The reaction is (45, 47, 48):



Thus, this reagent acts like a normal acid reacting with metallic ions.

The use of dimethylglyoxime (diacetyl dioxime) as a reagent for nickel, depends upon the following reaction (45, 48, 49, 50):



This reagent may be used for copper, bismuth and many other elements, the reaction being quantitative as well as qualitative, in many cases.

The use of aluminon and alizarin S (blue) in the test for aluminum is not well understood as yet. Engelder (11, 48) suggests that the dyestuff forms chelate rings as in the above cases, making use of coordinate linkages and forming definite compounds with the aluminum hydroxide. Others, however, believe that these dyes are merely adsorbed on the surface of the aluminum hydroxide and thus render the precipitate more visible.

PART III

ANALYTICAL PROCEDURE—CATIONS

GROUP SEPARATION—CATIONS

The usual sample of unknown may contain any number of metals which will give such varied results with a given reagent as to make it impractical to identify any one of them as long as certain others are present. For this reason it is necessary to treat the mixture in such fashion as to separate the ions present into groups, each containing only certain metals, and then further to subdivide each group until each metal is obtained in a solution free of interfering ions. This final solution is then tested with the proper reagent to show the presence or absence of that particular metallic ion. It is obvious, therefore, that such separations must be as complete as possible, for if a small amount of some metallic ion gets into the wrong group, false results are almost certain to be obtained. For this reason the following rules *must* be observed.

1. *Every detail* of the instructions must be followed in each step of the procedure. Appended notes must be carefully read, as they contain important hints that will save much trouble.

2. Clean apparatus and distilled water must be used at all times since many of the tests are extremely sensitive and a trace of foreign matter may ruin the whole analysis.

3. All precipitations must be complete—in other words, care must be taken to add enough reagent to react with all the ions that are to be precipitated at that point. Failure to do this means that the analysis of subsequent groups will be ruined owing to the presence of the ions that have not been precipitated because of insufficient reagent. On the

other hand, excess reagent must be avoided, too, as in many cases an excess of the reagent will redissolve all, or part of, the precipitate, with the result that the metallic ion appears in the next group and ruins the separation. To avoid adding either excess or insufficient reagent, it is desirable to use the following procedure.

First, add a couple of drops of reagent and stir the mixture thoroughly. If a precipitate forms, centrifuge, then to the clear supernatant liquid add another drop of reagent. If a precipitate forms in the liquid, add one more drop of reagent and stir once more. Centrifuge and repeat the above procedure until, on addition of a drop of reagent, no more precipitate forms in the clear layer of liquid. This marks the point when exactly enough reagent has been added.

If, on addition of the first two drops of reagent, no precipitate forms at once, it is well to rub the inside of the container with a stirring rod for about 1 min. and let the solution stand for a few minutes as the solution may be supersaturated.

4. Tongs and other metallic objects must not be touched to the tops of containers as acid fumes may attack them and a little of the resulting compound may get into the unknown solution and contaminate it.

5. Droppers must *not* be dipped into reagent bottles, nor must the droppers in the pipette-type reagent bottles ever be touched to the vessels used for analysis. A single failure to observe this rule may easily ruin all analyses—your own, as well as those of the rest of the class—for the rest of the semester. The dropper will almost certainly pick up some contamination and, when placed in the reagent again, will contaminate it too.

Before a complete analysis can be made, it is necessary that the unknown be in solution. In class work, it is customary to issue the unknown in the dissolved state. However, in industrial work such is often not the case, and

it is necessary to dissolve the material. A solid sample must, therefore, be treated first according to the procedure outlined in Part A. It is important that each step be carried out in the order given, as otherwise complications will arise.

Part A. Treatment of Solid Samples. 1. To about 50 mg. of the powdered solid unknown add 10 drops cold water. Heat almost to the boiling point, stir, and let stand until no more solid disappears. Filter, and save the liquid. If much solid seems to dissolve, repeat the treatment with water, combining the filtrates (see Note 1).

2. To any residual solid from (1) add 6*N* HNO₃ and treat as before. Again filter and save the liquid (see Note 2).

3. To any residual solid from (2) add concentrated HNO₃, and repeat the rest of the procedure in (2).

4. To any residual solid from (3) add aqua regia (made by mixing 6 drops dilute HCl with 2 drops concentrated HNO₃) and repeat the procedure outlined before (see Notes 3 and 4).

5. Any dark residual solid from (4) should be carefully dried in the air bath and cooled. Mix this with three times its volume of a mixture of 1 part Na₂O₂ and 3 parts Na₂CO₃. This mixture is then placed in a porcelain crucible (see Note 5) and heated over a strong Bunsen flame, to redness, holding it at that temperature for 10 to 15 min. The fused mixture is then allowed to cool, after which it is pulverized with the tip of a heavy glass rod and the resulting powder is put through the first three steps outlined earlier. Any residue remaining after that may, as a rule, be discarded (see Note 6).

Part B. Separation of a General Unknown into Groups. The separation of the metallic ions in a solution into groups for analysis is based upon five properties of the metallic compounds.*

* It would be impractical to cover the analysis of all known metals in a text of this scope. For that reason, only those metals listed here will be

1. The chlorides of all metals *except* silver, mercurous mercury, Hg_2^{++} , and lead are fairly soluble.

2. The sulfides of Hg, Cu, Pb, Cd, Sb, Sn, As, and Bi are insoluble in 0.3*N* HCl whereas the sulfides of the other metals are soluble in this concentration of acid.

3. The sulfides of Fe, Ni, Co, Mn, and Zn are soluble in 0.3*N* HCl but are insoluble in very slightly basic solution. The sulfides of Ba, Ca, Sr, K, Na, and Mg are soluble in either acid or slightly basic solutions.

4. The hydroxides of Al and Cr are precipitated by the basic solution required for the precipitation of the sulfides of Fe, Ni, Co, Mn, and Zn. The hydroxides of Ba, Ca, Sr, Mg, Na, and K are not precipitated by this weakly basic solution, the latter two being very soluble even in strongly basic solutions.

5. The carbonates of Ba, Sr, and Ca are only slightly soluble in either water or basic solutions buffered with ammonium salts. The carbonate of Mg is insoluble in water but is soluble in highly buffered basic solutions.

These properties enable us to separate the metals into five groups. The groups consist of the following metals:

Group I. Ag^+ , Hg_2^{++} , Pb^{++}

Group II. Cu^{++} , Pb^{++} , Hg^{++} , Cd^{++} , Sb^{+++} , Sb^{++++} , As^{+++} , As^{++++} , Bi^{+++} , Sn^{++} , Sn^{++++}

Group III. Fe^{+++} , Al^{+++} , Cr^{+++} , Ni^{++} , Co^{++} , Mn^{++} , Zn^{++}

Group IV. Ba^{++} , Sr^{++} , Ca^{++}

Group V. Mg^{++} , Na^+ , K^+ , NH_4^+

The method of precipitating these metals into their respective groups and of further separating and identifying them will be outlined in succeeding pages. The procedure will be given in outline form for clarity, and, for economy of space, abbreviated sentences will be used throughout.

studied, their analysis serving to cover those metals most commonly expected in commercial work, as well as serving to illustrate the principles involved in analysis. For a more comprehensive scheme of analysis see "Analytical Chemistry, Qualitative Analysis" vol. I, by Treadwell and Hall, John Wiley & Sons, Inc., New York.

The outline will describe the method of precipitating each group and analyzing it. To analyze a general unknown, it is necessary only that the solution left from the Group I precipitation be used as the unknown for the Group II analysis; the solution from the Group II precipitation, for the Group III unknown, etc.

For a general unknown, *no more* than 1 ml. of unknown should be taken. More will make the analysis difficult. In the case of group unknowns, 8 to 10 drops is sufficient.

GROUP I METALS

CHEMICAL CHARACTERISTICS

Silver. Metallic silver is rather inactive chemically. It does not react with dilute nonoxidizing acids or with alkalies. It reacts with aqua regia, but forms a mass of AgCl that is very difficult to dissolve. The best solvent for this metal is HNO_3 .

Compounds of Silver. Silver forms a large number of complex ions and slightly soluble compounds. A few of its most characteristic reactions are: Soluble chlorides give AgCl, white, insoluble in water or HNO_3 , but soluble in NH_4OH forming $\text{Ag}(\text{NH}_3)_2^+$, in concentrated HCl, KCl or NaCl solution forming AgCl_2^- , and in alkali cyanides forming $\text{Ag}(\text{CN})_2^-$ ions. H_2S precipitates Ag_2S , black, the least soluble of the ordinary silver compounds, being insoluble in water, HCl or NH_4OH , but soluble in dilute HNO_3 and in concentrated alkali cyanides. The fluoride is very soluble in water. Bromides precipitate AgBr, pale yellow, insoluble in water or HNO_3 ; slightly soluble in NH_4OH , very soluble in alkali cyanides. NaI or KI precipitates AgI, yellow, insoluble in water, HNO_3 , or NH_4OH ; soluble in alkali cyanides. All the halides of silver are soluble in solutions of $\text{Na}_2\text{S}_2\text{O}_3$. Na_2CO_3 precipitates Ag_2CO_3 , white, insoluble in water; soluble in NH_4OH and HNO_3 . NaOH, KOH and NH_4OH give AgOH ($2\text{AgOH} \rightleftharpoons \text{Ag}_2\text{O} + \text{H}_2\text{O}$) black or brown, insoluble in water but

soluble in HNO_3 or in excess NH_4OH . Ag_2O is a good oxidizing agent, being itself reduced to metallic silver.

Lead. Metallic lead is attacked by all the common acids. Owing to the fact that most lead compounds are insoluble, however, it is best dissolved in dilute HNO_3 . The nitrate and acetate are its most soluble compounds.

Compounds of Lead. The following reagents, added to solutions of $\text{Pb}(\text{NO}_3)_2$ give compounds that are insoluble in water: H_2S gives PbS , black, insoluble in water, NH_4OH , dilute HCl , $(\text{NH}_4)_2\text{S}$, and Na_2S_x ; soluble in $2N$ HNO_3 and in concentrated HCl .

Soluble chlorides give PbCl_2 , white, only slightly soluble in cold water, but soluble in hot water and in strong HCl . Iodides give PbI_2 , yellow, and less soluble than PbCl_2 ; soluble in concentrated alkali iodides, forming PbI_3^- ions.

KOH or NaOH precipitates $\text{Pb}(\text{OH})_2$, white, insoluble in water or NH_4OH ; soluble in HNO_3 , acetic acid, or excess alkali (forming HPbO_2^-); forming insoluble, brown PbO_2 on addition of H_2O_2 , hypochlorites, or other oxidizing agents.

H_2SO_4 or sulfates precipitate PbSO_4 , white, insoluble in water; soluble in concentrated H_2SO_4 [forming soluble $\text{Pb}(\text{HSO}_4)_2$], in strong ammonium or sodium acetate solution [forming slightly ionized $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$], and in strong alkalis.

K_2CrO_4 and other soluble chromates precipitate PbCrO_4 , yellow, insoluble in water or acetic acid; soluble in HNO_3 and alkalis.

Mercury. Metallic mercury is very inactive, being between copper and silver in the displacement series. As it is below hydrogen, it does not react with dilute H_2SO_4 or HCl . It dissolves readily, however, in hot HNO_3 to form $\text{Hg}(\text{NO}_3)_2$, or in cold HNO_3 to form $\text{Hg}_2(\text{NO}_3)_2$.

HI dissolves mercury readily, forming hydrogen and the slightly dissociated HgI_4^- ion. Hot, concentrated H_2SO_4 dissolves mercury forming the sulfate and SO_2 .

Compounds of Mercury. Mercury forms compounds of two types—mercurous, Hg_2^{++} , and mercuric, Hg^{++} . The nitrates of both are soluble, but in many ways their reactions are so different as to make it necessary to consider them separately.

Mercurous Compounds. Soluble chlorides precipitate Hg_2Cl_2 , white, insoluble in water or dilute acids; soluble in hot, strong HNO_3 or H_2SO_4 . With NH_4OH , $\text{Hg}_2(\text{NO}_3)_2$ gives a mixture of white $\text{Hg}_2\text{O}(\text{NH}_2)(\text{NO}_3)$ and metallic mercury. Alkali carbonates give a yellow precipitate of Hg_2CO_3 , decomposed on boiling or standing, into a gray mixture of Hg and HgO . H_2S precipitates a mixture of HgS and Hg, the whole precipitate being soluble in Na_2S_x . KI precipitates green Hg_2I_2 , which reacts with excess KI to form HgI_4^- and Hg. Copper displaces Hg_2^{++} ions from their compounds.

Mercuric Compounds. Soluble iodides precipitate HgI_2 , red, insoluble in water but soluble in excess alkali iodide to form HgI_4^- . HgBr_2 is more soluble in water than is HgI_2 . HgCl_2 is fairly soluble. $\text{Hg}(\text{NH}_2)\text{Cl}$, white, insoluble in water, is formed by treating Hg_2Cl_2 or HgCl_2 with NH_4OH . It is soluble in hot NH_4Cl [forming $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$] and in acids.

HgO , red or yellow, is insoluble in water but soluble in acids. It is precipitated when hot solutions containing Hg^{++} are treated with KOH or NaOH , or with Na_2CO_3 or K_2CO_3 . Unstable above 300°C . giving metallic mercury and oxygen.

HgCrO_4 , orange, is insoluble in water, soluble in acids. It is precipitated by adding neutral alkali chromates to solutions containing neutral or acid-buffered Hg^{++} .

KSCN precipitates $\text{Hg}(\text{SCN})_2$, white, insoluble in water; soluble in excess KSCN or NH_4SCN , forming $\text{Hg}(\text{SCN})_4^-$. H_2S precipitates HgS , black, insoluble in water, dilute acids, concentrated HCl or $(\text{NH}_4)_2\text{S}$. Soluble in hot, concentrated HNO_3 (with long boiling), in aqua regia, in yellow

$(\text{NH}_4)_2\text{S}_x$, and in Na_2S (forming HgS_2^- from which it is reprecipitated by acidification). When it is precipitated from solutions of Hg^{++} , the first substance to form is a white, insoluble double salt of the type, $(\text{HgS})_2 \cdot \text{HgCl}_2$. This is slowly converted, by more H_2S , into black HgS . Dissolving HgS in HNO_3 produces $(\text{HgS})_2 \cdot \text{Hg}(\text{NO}_3)_2$ as an intermediate product, this slowly dissolving to form the normal nitrate.

ANALYTICAL ASPECTS

It will be recalled that the chlorides of the three ions— Ag^+ , Hg_2^{++} , and Pb^{++} —are insoluble whereas those of other metallic ions are soluble. It is possible, therefore, to separate these three metals from the others in a general unknown by adding chloride ions to the solution. This precipitates the chlorides of lead, silver, and mercurous mercury, leaving the other metallic ions in solution. A solution of HCl will furnish the necessary chloride ions without adding anything undesirable to the solution. Too great excess, however, will redissolve part of the precipitate, forming PbCl_3^- and AgCl_2^- .

The further separation and identification of these three metals depend upon (1) the high solubility of lead chloride in hot water and the low solubility of lead chromate; (2) the high solubility of silver chloride in ammonium hydroxide and its reprecipitation on the addition of nitric acid; and (3) the reaction between mercurous chloride and ammonium hydroxide to form a mixture of free mercury and mercuric aminochloride (HgNH_2Cl).

PRELIMINARY EXPERIMENTS—GROUP I

1. Silver ion, Ag^+ . *a.* To 2 drops of a solution containing Ag^+ ions, add 1 drop 1N HCl solution. Filter*

* See Semi-micro Technique—Filtrations. Use the technique described there, whenever the instructions say to filter.

and try dissolving a small portion of the precipitate from (a) in hot water.

Try dissolving a second portion of the precipitate in concentrated HCl.

b. To another portion of the precipitate from (a) add 2 drops 6*N* NH₄OH and stir. If any solid refuses to dissolve, filter. Place 1 drop of the clear filtrate on a small watch glass, place the latter on a black surface, and add 2 drops 6*N* HNO₃.

To another drop of the ammoniacal solution add 1 drop 0.1*N* KI solution.

To a third drop of the ammoniacal solution add 1 drop rhodanine solution and 2 drops 6*N* HNO₃. This test is capable of detecting as little as 0.001 mg. of Ag⁺ (51, 13).

c. To 1 drop Ag⁺ test solution add 1 ml. water and stir thoroughly. Now place 2 drops of this solution in a microbeaker and add 1 drop 3*N* K₂CrO₄ solution.

Place another drop of the diluted test solution on a piece of filter paper. To the same spot add 1 drop 3*N* K₂CrO₄ solution. Compare the two results (Question 1).

2. Lead Ion, Pb⁺⁺. a. To 2 drops Pb⁺⁺ test solution add 1 drop 1*N* HCl solution. Filter and wash the precipitate in cold water.

To a small portion of the precipitate add 2 to 3 drops cold HCl.

To the rest of the precipitate add 5 drops hot water. Heat on the steam bath to make sure the solution is hot and notice whether lead chloride seems to be soluble in hot water (Question 2).

b. To 2 drops of the hot solution from (a) on a watch glass add 1 drop 6*N* H₂SO₄. Place against a black background for observation purposes.

c. Repeat (b), using 3*N* K₂CrO₄ solution instead of H₂SO₄.

d. To half of the PbCrO₄ from (c) add 2 drops 6*N* HNO₃. To the second half of the precipitate add 2 drops 6*N* NaOH solution.

e. To 1 drop Pb^{++} test solution on a filter paper add *in the order mentioned* 1 drop H_2O_2 and 1 drop NH_4OH . Warm for 1 min. in a jet of steam from the steam bath. Examine the color of the spot on the paper. The reaction that has taken place is:



Now, to this spot add 1 drop benzidine reagent. Note the new color that appears. PbO_2 is an oxidizing agent; and, when benzidine reacts with an oxidizing agent, it forms a complex organic dye of the color observed. Consequently, this test is not specific for lead—any oxidizing agent will give a similar test. Taken at this point, however, with other elements eliminated, it is a good confirmatory test for lead, being capable of detecting 0.0015 mg. lead (14).

f. To 2 drops Pb^{++} test solution add 1 drop 0.1N KI solution. Heat to boiling, noting all occurrences, then cool.

3. Mercurous Ion, Hg_2^{++} . a. To 2 drops Hg_2^{++} test solution add 1 drop 1N NH_4Cl solution. Filter and wash the precipitate with cold water.

Try dissolving part of the precipitate in 5 drops hot water.

Try dissolving another portion of the precipitate in 2 drops 6N NH_4OH .

b. To some of the precipitate from (a) add 2 drops 6N NH_4OH . Note what occurs. Filter and wash precipitate in cold water.

To this precipitate add 8 drops aqua regia (a mixture of 1 part concentrated HNO_3 with 3 parts 6N HCl) and evaporate to dryness. To the residue add 3 drops of a saturated solution of sodium acetate, stir, and add 2 drops diphenylcarbazide reagent. Note the results (see Note 8 and Question 3).

c. To 4 drops Hg_2^{++} test solution add 1 drop 0.1N KI solution. Note the color of the precipitate formed. Now

GROUP I ANALYSIS

For the systematic analysis of an unknown, the following procedure may be followed (see Note 84).

To the group or general unknown, add 2 drops 1N HCl solution, stir thoroughly and centrifuge. Test for completeness of precipitation and add more reagent if necessary (see Note 9). Stir once more, then filter (centrifuge). Wash precipitate with *cold* water.

Filtrate. Save for Groups II, III and IV.

Precipitate (see Note 10). Consists of PbCl_2 , Hg_2Cl_2 and AgCl . Add 5 drops boiling water and heat (while stirring) on steam bath until almost boiling (see Note 11). Centrifuge *quickly* and immediately remove filtrate. Repeat washing until wash water gives no test for lead.

Filtrate. Contains PbCl_2 . While still hot, put 1 drop on a filter paper and add 1 drop 3% H_2O_2 , 1 drop dil. NH_4OH , heat over steam bath for 1 min. then add 1 drop ben-zidine reagent.

BLUE COLOR

indicates Pb^{++} present.

To 1 drop K_2CrO_4 soln. on a black background add 1 drop of the hot filtrate.

YELLOW PPT.*

proves Pb^{++} present.

Precipitate. Consists of Hg_2Cl_2 and AgCl . Add 3-4 drops of dil. NH_4OH and stir. Centrifuge.

Filtrate. Contains $\text{Ag}(\text{NH}_3)_2\text{Cl}$. To 1 drop of filtrate on a watch glass over a black background add 1 drop conc. HNO_3 .

WHITE CLOUDY PPT. indicates Ag^+ present.

To 1 drop of filtrate on a spot plate add 1 drop rhodamine reagent and 1 drop 6N HNO_3 .

RED PPT.

confirms Ag^+ present.

To 1 drop of filtrate on a watch glass add 1 drop 0.1N KI soln.

PALE YELLOW PPT. proves Ag^+ present.

Precipitate. BLACK or GRAY PPT.

of Hg and HgNH_2Cl proves Hg_2^{++} present.

To the precipitate add 5 drops freshly prepared aqua regia and evaporate to dryness. Dissolve residue in 5 drops saturated sodium acetate soln., add 1 drop dil. acetic acid and 1 drop of a *freshly* prepared alcoholic soln. of gallic acid.

YELLOW or ORANGE PPT.

confirms Hg_2^{++} present (see Note 12).

* In many places it will be necessary to use the abbreviation "PPT" for "precipitate" in order to conserve space.

try to redissolve this precipitate by adding excess KI (using a saturated solution of KI for this purpose).

d. To 1 drop Hg_2^{++} test solution add 1 drop 1N acetic acid, 1 drop saturated sodium acetate solution, and 1 drop of a freshly prepared alcoholic solution of gallic acid (see Note 12). This test is specific for mercury (Hg_2^{++} or Hg^{++}) in the presence of any of the metals of Groups I and II except silver, the latter giving a dark coloration.

GROUP II METALS

CHEMICAL CHARACTERISTICS

Copper. Metallic copper is much like mercury in its reactions. It is insoluble in dilute, nonoxidizing acids *in absence of air*, but dissolves slowly in strong HCl, if air is present, to form the complex cuprochloride ion, Cu_2Cl_4^- . It dissolves readily in HNO_3 and in hot, concentrated H_2SO_4 . Copper displaces mercury and silver from their compounds.

Two types of copper compounds are formed.

Cuprous Compounds. These are similar to silver and mercurous compounds in many respects. The chloride, Cu_2Cl_2 , is white, insoluble in water; soluble in HCl, forming Cu_2Cl_4^- , and in excess NH_4OH , forming $\text{Cu}_2(\text{NH}_3)_4^{++}$. With NaOH, solutions of Cu_2^{++} give a yellow precipitate of $\text{Cu}_2(\text{OH})_2$, decomposed, on boiling, into red Cu_2O . With H_2S , black Cu_2S is precipitated, insoluble in dilute non-oxidizing acids but readily soluble in warm HNO_3 to form $\text{Cu}(\text{NO}_3)_2$.

Cupric Compounds. With solutions of Cu^{++} , H_2S precipitates black CuS , insoluble in dilute, nonoxidizing acids, and only slightly soluble in $(\text{NH}_4)_2\text{S}$; readily soluble in warm HNO_3 , or excess KCN [forming $\text{Cu}(\text{CN})_3^-$ ions]. With NaOH, solutions of Cu^{++} give green $\text{Cu}(\text{OH})_2$, insoluble in water but soluble in excess NH_4OH [giving deep blue $\text{Cu}(\text{NH}_3)_4^{++}$], in KCN, and in acids. With Na_2CO_3 , a

basic carbonate is precipitated, soluble in acids and in NH_4OH . Its nitrate, sulfate and chloride are very soluble in water.

Bismuth. Bismuth is a rather inactive metal, insoluble in HCl or cold H_2SO_4 , but soluble in HNO_3 or hot H_2SO_4 . The element exhibits two principal valences, +3 and +5. The trivalent form is the most stable.

Compounds of Bismuth. The compounds of bismuth hydrolyze readily in dilute solutions giving white precipitates of the type BiOCl or, $\text{BiO}(\text{NO})_3$. Some characteristic reactions of bismuth ion solutions are:

NaOH gives white $\text{Bi}(\text{OH})_3$, insoluble in water or excess NaOH ; soluble in acids.

Alkali carbonates precipitate basic carbonates of the type $\text{Bi}(\text{OH})\text{CO}_3$. $\text{K}_2\text{Cr}_2\text{O}_7$ gives yellow $(\text{BiO})_2\text{Cr}_2\text{O}_7$, soluble in strong acids but insoluble in alkalies.

H_2S precipitates Bi_2S_3 , brown, insoluble in dilute, non-oxidizing acids or $(\text{NH}_4)_2\text{S}$; soluble in hot concentrated HCl or in dilute HNO_3 .

Metallic zinc, or stannite ions, HSnO_2^- , will reduce Bi^{+++} to metallic bismuth, usually as a black powder. Soluble iodides precipitate black BiI_3 , soluble in excess to form yellow BiI_4^- .

Strong oxidizing agents such as Cl_2 , ClO^- , or H_2O_2 , added to alkaline suspensions of $\text{Bi}(\text{OH})_3$ give a brown precipitate of meta-bismuthic acid, HBiO_3 , insoluble in water, but a powerful oxidizing agent.

Cadmium. The metal is moderately active, easily volatilized element (B.P., 767°C). On heating, it combines with oxygen to form brown CdO ; it dissolves slowly in HCl or H_2SO_4 , and rapidly in HNO_3 .

Compounds of Cadmium. CdS is yellow or orange in color; insoluble in $(\text{NH}_4)_2\text{S}$, Na_2S_x , or KCN ; soluble in $3N$ HCl , HNO_3 , and in hot, dilute H_2SO_4 .

With solutions of Cd^{++} , NaOH precipitates white $\text{Cd}(\text{OH})_2$, insoluble in excess alkali; soluble in acids, or in

NH_4OH [forming $\text{Cd}(\text{NH}_3)_4^{++}$ ions]. Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$ forms white CdCO_3 , insoluble in water; soluble in acids, in KCN , and in solutions of ammonium salts. $\text{K}_4\text{Fe}(\text{CN})_6$ precipitates white $\text{Cd}_2\text{Fe}(\text{CN})_6$. The nitrate, chloride, and sulfate of cadmium are soluble in water.

Arsenic. Metallic arsenic is a gray very brittle substance, subliming readily at 615°C . giving a characteristic garlic-like odor. Its vapors and compounds are extremely poisonous. The element is amphoteric, its oxides dissolving in acids or in alkalis. The element does not dissolve in HCl , but dissolves slowly in strong alkalis, and more rapidly in NaOCl , aqua regia, or concentrated HNO_3 . At high temperatures it combines readily with sulfur, oxygen, and chlorine and reacts with metals to form arsenides of the type Zn_3As_2 .

Compounds of Arsenic. Arsenic exists in both the trivalent and the pentavalent state. If in alkaline solution, the arsenic is present in the form of arsenite or arsenate ions; if in acid solution, as arsenious or arsenic ions. The two valence types will be discussed separately. Both types give arsine (AsH_3 , a very poisonous gas) on reduction with acid and zinc or aluminum, or on reduction with alkalis and zinc or aluminum. Trivalent arsenic compounds are the most easily reduced, however.

Arsenious Compounds and Arsenites. As_2O_3 , white, is slightly soluble in water, but very soluble in HCl forming As^{+++} , and in alkalis forming $\text{AsO}_3^=$, or arsenite ions. H_2S causes no precipitation from neutral or alkaline solutions of arsenites, owing to formation of soluble thioarsenites. From slightly acid solutions of arsenites, H_2S precipitates As_2S_3 , yellow, insoluble in dilute, nonoxidizing acids, but soluble (with long boiling) in concentrated HCl , and readily soluble in concentrated HNO_3 , aqua regia, or ammoniacal H_2O_2 , forming $\text{AsO}_4^=$; in ammonium carbonate, forming a mixture of $\text{AsS}_3^=$ and $\text{AsO}_3^=$; in alkali sulfides, forming $\text{AsS}_3^=$; and in Na_2S_x , forming $\text{AsS}_4^=$.

AgNO_3 , with neutral or faintly acid solutions of arsenites gives Ag_3AsO_3 , yellow, insoluble in water, but readily soluble in NH_4OH or HNO_3 .

AsH_3 (see above) decomposes on heating, giving As and H_2 . This is the basis of the Marsh test for arsenic.

Arsenic Compounds and Arsenates. As_2O_5 dissolves readily in water to form arsenic acid, H_3AsO_4 , and in alkalis to form arsenates.

H_2S does not form any precipitate with neutral solutions of arsenates. With weakly acid solutions, it will form As_2S_5 only after a long period of time. However, if the solution of arsenate is first made strongly acid with HCl , yellow As_2S_5 precipitates at once.*

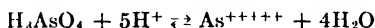
As_2S_5 is insoluble in water or nonoxidizing acids. It is soluble, however, in the same solvents as those listed for As_2S_3 .

AgNO_3 gives, with neutral solutions of arsenates, Ag_3AsO_4 , chocolate colored, insoluble in water but soluble in NH_4OH and in acids.

Ammonium molybdate gives $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$, yellow, insoluble in water or dilute HNO_3 , but readily soluble in NH_4OH or alkalis. Excess reagent is needed for the precipitation.

Magnesia mixture (a mixture of MgCl_2 , NH_4OH , and NH_4Cl) precipitates white crystalline $\text{MgNH}_4\text{AsO}_4$, insoluble in water or dilute NH_4OH . Arsenites give no precipitate with this reagent.

* The failure of H_2S to precipitate the sulfides from neutral or weakly acid solutions of arsenates is due partly to the formation of soluble complex thioarsenate ions (such as AsS_4^- , AsO_3S^- , etc.), and partly to the fact that H_3AsO_4 is quite stable and gives a very low concentration of As^{+++} . A high concentration of H^+ , however, favors the formation of As^{++++} in accordance with the equation



Therefore, since As_2S_5 is insoluble in concentrated HCl , As_2S_5 precipitates readily from solutions of strong HCl .

Slightly acid solutions of arsenates give a yellow precipitate of As_2S_5 when heated with $\text{Na}_2\text{S}_2\text{O}_3$. Arsenites give a similar precipitation.

Antimony. Metallic antimony is a brittle, silvery metal, with a melting point of 630°C ., a boiling point of 1380°C ., and a density of 6.7. At high temperatures, antimony combines readily with oxygen to form Sb_2O_3 and Sb_2O_4 , with sulfur to form Sb_2S_3 ; and with chlorine to form SbCl_3 and SbCl_5 . It does not dissolve in nonoxidizing acids, but dissolves readily in aqua regia. HNO_3 attacks it, but forms an oxide that is soluble, with great difficulty, in concentrated HNO_3 .

Compounds of Antimony. Though antimony exists in both the tri- and pentavalent states, the trivalent compounds are the most stable. Both oxides are amphoteric, but Sb_2O_3 is more basic and Sb_2O_5 is more acidic in nature. Antimonic compounds are oxidizing agents.

All antimony salts hydrolyze in dilute solution, SbCl_3 giving SbOCl and $\text{Sb}(\text{OH})_3$, both of them white, insoluble in water, but soluble in acids and alkalis. Tartrates repress the precipitation, forming soluble $(\text{SbO})\text{C}_4\text{H}_4\text{O}_6^-$.

NaOH , NH_4OH and alkali carbonates precipitate antimony hydroxide, $\text{Sb}(\text{OH})_3$, white, soluble in acids or strong alkalis. H_2S precipitates Sb_2S_3 , orange, insoluble in dilute nonoxidizing acids, but soluble in strong HCl ; in $(\text{NH}_4)_2\text{S}$, forming SbS_3^- ; and in alkalis forming mixtures of thio- and oxythio-antimonite ions.

Zinc and acid reduce antimony compounds to stibine, SbH_3 , a gas giving reactions very similar to those of arsine, AsH_3 . Stibine is not formed in alkaline solution, however, this being used as a method of identifying arsenic in the presence of antimony. The Marsh test gives a mirror of metallic Sb, which is distinguished from the As mirror by the fact that Sb is not soluble in NaOCl solution.

Tin. Metallic tin is a soft, malleable metal, having a melting point of 232°C ., a boiling point of 2270°C ., and a

density of 7.3. Being just above hydrogen in the displacement series, it slowly dissolves in dilute nonoxidizing acids, and, more readily, in strong, hot, concentrated HCl. The metal reacts with HNO_3 to form meta-stannic acid, H_2SnO_3 , a white substance, insoluble in alkalis or acids. In neutral or slightly acid solutions, zinc displaces tin from its compounds, forming the metal.

Compounds of Tin. Tin forms compounds in which it has a valence of two and of four. The latter are the most stable as air readily oxidizes the former to the tetravalent state. Both forms are amphoteric, and the compounds of both hydrolyze readily in dilute aqueous solutions. Most of the analytical reactions make use of the bivalent form.

Stannous Compounds. With NH_4OH , carbonates, and alkalis, white $\text{Sn}(\text{OH})_2$ is precipitated; only slightly soluble in excess NH_4OH but readily soluble in excess alkali [forming stannite (HSnO_2^-) ions], and in mineral acids. Stannites decompose slowly, on standing, (or more rapidly if heated) giving brown SnO and metallic tin.

SnCl_2 (the most common stannous compound) hydrolyzes in water giving $\text{Sn}(\text{OH})\text{Cl}$, or in more dilute solutions giving $\text{Sn}(\text{OH})_2$. Solutions of SnCl_2 are kept stable by adding HCl to prevent hydrolysis, and metallic tin, to reduce any stannic ions formed by air oxidation.

H_2S precipitates SnS , brown, insoluble in water or $(\text{NH}_4)_2\text{S}$, but soluble in moderately strong HCl, in mixtures of oxalic acid and ammonium salts, and in alkali or ammonium polysulfide forming thiostannate (SnS_3^-) ions. The latter decompose on acidification giving SnS_2 .

All stannous compounds are good reducing agents. They reduce HgCl_2 to Hg_2Cl_2 , then to free Hg. Bismuth compounds are reduced by alkaline stannous solutions to black metallic Bi. Alkaline solutions of lead are reduced, in a similar manner, to metallic Pb, the reaction being much slower than with bismuth compounds. Stannous compounds will also reduce ferric ions to the ferrous state.

Stannic Compounds. The simple stannic ion seldom exists in solution as it has strong tendencies to form complex negative ions. In neutral aqueous solutions, stannic compounds hydrolyze, forming $\text{Sn}(\text{OH})_4$. To prevent this the solution must be strongly acid, the tin being in the form of ions of the type, SnCl_6^- . Alkalies, NH_4OH or soluble carbonates precipitate $\text{Sn}(\text{OH})_4$ from solutions of stannic compounds. The $\text{Sn}(\text{OH})_4$ thus formed is white, insoluble in NH_4OH or Na_2CO_3 , but soluble in alkalies or K_2CO_3 (forming $\text{Sn}(\text{OH})_6^-$) and in mineral acids. If the stannic hydroxide is allowed to stand, or is heated for a while, it is converted to meta-stannic acid (H_2SnO_3) which is insoluble in either acids or alkalies.*

H_2S reacts with solutions of stannic compounds, precipitating SnS_2 , yellow, insoluble in water or ammonium carbonate; soluble in $(\text{NH}_4)_2\text{S}$ or alkali polysulfides (forming SnS_3^-) and in acids. Considerable amounts of oxalic acid prevent this precipitation.

Antimony, lead, or iron reduces acid solutions of stannic compounds to the stannous state but not to the metal. Zinc reduces stannic solutions to metallic tin; but if the solution is strongly acid, the tin redissolves, forming stannous ion.

Stannic compounds are not reducing agents.

ANALYTICAL ASPECTS

Group II consists of those metals whose sulfides can be precipitated by H_2S in a solution whose acidity is equal to that of 0.3*N* HCl . The metals of this group are divided

* For one method of dissolving meta-stannic acid (sometimes called β -stannic acid), see the section on Amphoterism (also see Note 4).

Besides the method given in these sections a very effective method of putting meta-stannic acid into solution is to fuse it with Na_2CO_3 and sulfur, treating the pulverized residue with water. The reaction is



On weakly acidifying this solution, SnS_2 will precipitate.

into two subgroups on the basis of the solubility of their sulfides in $(\text{NH}_4)_2\text{S}$ reagent. Subgroup *A* (sometimes called the "copper group") consists of those metals whose sulfides are *not* soluble in $(\text{NH}_4)_2\text{S}$, *i.e.*, copper, lead, mercuric mercury, cadmium and bismuth; subgroup *B* (the "tin group") consists of those metals whose sulfides *are* soluble in $(\text{NH}_4)_2\text{S}$, *i.e.*, tin, arsenic, and antimony.

Lead is considered in this group as well as in Group I because its chloride is not extremely insoluble (it is about a thousand times as soluble as silver chloride) and some lead remains in solution and is precipitated as PbS in Group II.

PRELIMINARY EXPERIMENTS—GROUP II*

1. **Mercuric Ion, Hg^{++} .** *a.* Pass H_2S through 2 drops Hg^{++} test solution for about 30 sec., noting the color changes. Filter and wash the precipitate. Divide the precipitate into two parts.

To one portion of the precipitate add 5 drops 3*N* HNO_3 and heat on the steam bath for about 3 min. (Question 4).

To the other portion of the precipitate add 5 drops freshly prepared aqua regia (Question 5) and evaporate to dryness. Cool, add 2 drops water, stir, then filter. To 1 drop filtrate on a watch glass add 1 drop SnCl_2 solution (see Note 13).

b. To 3 drops Hg^{++} test solution add 1 drop 0.1*N* KI solution. Now add an excess of saturated KI solution (Question 6).

c. To 2 drops Hg^{++} test solution add 1 drop 3*N* K_2CrO_4 solution.

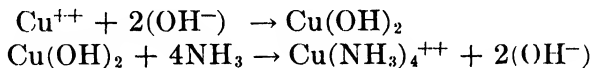
d. To 2 drops Hg^{++} test solution add 1 drop 1*N* NH_4Cl solution and 1 drop concentrated NH_4OH (Question 7).

e. To 1 drop Hg^{++} test solution add 1 drop freshly prepared solution of gallic acid in alcohol.

* For additional chemical properties that are occasionally used for tests for these metals, see Auxiliary Tests.

2. Copper Ion, Cu^{++} . *a.* Pass H_2S through 2 drops Cu^{++} test solution for about 30 sec. Filter and wash the precipitate. Divide into two parts.

To one portion of the precipitate add 5 drops 3*N* HNO_3 and heat. Filter off any sulfur (recognized by the fact that it usually floats whereas CuS sinks). To the clear solution add 1*N* NH_4OH , drop by drop, noting that a precipitate first forms, then dissolves in the excess reagent (see page 38). The reaction is*



To the second portion of precipitate add 5 drops freshly prepared $(\text{NH}_4)_2\text{S}$ solution. Warm on the steam bath (Question 8).

b. To 2 drops Cu^{++} test solution add 2 drops 6*N* NH_4OH . Then add, drop by drop until the deep blue color just disappears, a 3 per cent solution of KCN (*Caution:* KCN is an extremely dangerous poison. If added to acid solutions, it gives off very poisonous fumes of HCN . For this reason it is important that every detail in the procedure be checked before it is used.) Now bubble H_2S through the solution for a minute (see Note 14).

c. To 1 drop Cu^{++} test solution on a watch glass add 1 drop $\text{K}_4\text{Fe}(\text{CN})_6$ solution.

d. Put 1 drop Cu^{++} test solution on a bit of filter paper. To the same spot add 1 drop α -benzoinoxime solution. Hold the spot over a watch glass containing a few drops concentrated NH_4OH and observe any color change (52, 53).

3. Bismuth Ion, Bi^{+++} . Bismuth forms a sulfide under the same conditions as does copper. Like CuS , Bi_2S_3 is black in color and is soluble in 3*N* HNO_3 . To save time,

* An explanation of the reasons for NH_4OH acting as a source of both OH^- ions and NH_3 molecules, will be found on p. 38.

only a few of the other characteristic reactions of its ions will be tried experimentally.

a. To 1 drop Bi^{+++} test solution add 10 drops water and stir. Observe very closely as the resulting precipitate is almost transparent. If no precipitate appears, add 1 drop 6*N* NH_4OH (see Note 7 and Question 9).

b. To 1 drop Bi^{+++} test solution on a filter paper, add 1 drop 1*N* NaOH solution and 1 drop freshly prepared sodium stannite solution (see Note 15).

c. To 1 drop Bi^{+++} test solution add 1 drop Cu^{++} test solution and 10 drops water. Add 6*N* NH_4OH , drop by drop, until the whole solution is deep blue. Can you see any precipitate in the solution? Try to dissolve it by adding more NH_4OH (see Note 16).

d. To 1 drop Bi^{+++} test solution on a piece of filter paper add 1 drop cinchonine reagent. This test is capable of detecting as little as 0.00014 mg. of bismuth. Try the reagent on a drop of a mixture of Cu^{++} , Pb^{++} , Bi^{+++} , and Hg^{++} , noting the concentric rings (6, 14).

4. Cadmium Ion. a. Bubble H_2S through 2 drops Cd^{++} test solution until precipitation is complete. Filter and wash the precipitate. Divide the precipitate into two parts.

To one portion of the precipitate add 5 drops 3*N* HNO_3 and warm on the steam bath.

To the second portion of precipitate add 5 drops of 1:4 H_2SO_4 (a mixture of 1 drop concentrated H_2SO_4 and 4 drops water). Warm on the steam bath.

b. To 1 drop Cd^{++} test solution on a filter paper add 1 drop 1*N* NaOH solution. In the center of the spot, place a tiny crystal of thiosinamine (allyl thiourea), and heat in a jet of steam from the steam bath. A bright yellow spot should quickly result (16) (see Note 17).

c. To 1 drop Cd^{++} test solution add 1 drop Cu^{++} test solution and 4 drops water. Now add 2 drops concentrated NH_4OH ; then add 3 per cent KCN solution, drop by

drop, until the blue color of the copper is discharged. Bubble H_2S through this solution for a few seconds.

5. Arsenic Ion, As^{++++} . *a.* Pass H_2S through 2 drops As^{++++} test solution until a precipitate forms. Note the length of time it takes.

To 2 drops As^{++++} test solution add a small crystal of NH_4I , heat to boiling and pass H_2S through the solution. Note the length of time required before a precipitate forms this time (see Note 18). Continue passing in H_2S until precipitation is complete. Filter and wash the precipitate. Divide the precipitate into three portions.

To one portion of precipitate add 5 drops $(\text{NH}_4)_2\text{S}$ solution and warm. When solution is complete add, drop by drop, 1*N* HCl until the solution is faintly acid (see Note 19).

To another portion of the precipitate add 5 drops concentrated HCl and heat on the steam bath. Does the precipitate dissolve?

To the third portion of precipitate add 5 drops aqua regia and evaporate just to dryness (see Note 20). Dissolve the residue in 2 drops 6*N* HCl . Add 1 drop 0.1*N* sodium bisulfite and warm 1 min. Then add 5 drops 6*N* NaOH solution and stir. Transfer to the gas evolution apparatus. In the bulb of the latter place a bit of filter paper moistened with a drop of AgNO_3 solution and cover with a loose plug of cotton. Then, to the solution in the main tube, add four pieces arsenic-free granulated aluminum and quickly place the top of the apparatus in position. Warm if necessary and set aside for about 5 min. Then examine the silver nitrate spot (see Note 21).

6. Antimony Ion, Sb^{+++} . *a.* Pass H_2S into 2 drops Sb^{+++} test solution until precipitation is complete. Filter and wash precipitate. Divide the precipitate into two parts.

To one portion of the precipitate add 5 drops $(\text{NH}_4)_2\text{S}$ solution and warm on the steam bath. To the solution so

obtained add 1*N* HCl, drop by drop, until the solution is faintly acid.

To the second portion add 5 drops concentrated HCl and heat until the precipitate dissolves. Now add 5 drops cold water and pass in H₂S for 1 min.

b. To 1 drop Sb⁺⁺⁺ test solution add 5 drops water. Now try to redissolve the precipitate formed, by adding concentrated HCl (see Note 22).

c. To 1 drop Sb⁺⁺⁺ test solution add 1*N* NaHCO₃ solution, drop by drop, until a precipitate barely begins to form. Add just enough 6*N* HCl to redissolve the precipitate, heat almost to boiling, and add a crystal of sodium thiosulfate. Note the orange precipitate of antimony oxysulfide, SbOS₂ (54, 55).

GROUP II ANALYSIS

The unknown may be the filtrate from the precipitation of the chlorides of Group I, or a solution provided by the instructor.

Evaporate *barely* to dryness then *cool* (see Note 25). Add 1 drop of conc. HCl, let stand 1 min. then add 1 ml. water (see Note 26) and pass in H₂S until precipitation is complete (see Note 34). Add a small crystal of NH₄I, heat to boiling, and again pass in H₂S. Cool once more and complete the precipitation with H₂S (see Question 10). Filter and wash precipitate *twice* with NH₄NO₃·H₂S solution (see Notes 27 and 28).

Filtrate. Make strongly acid with HCl and boil to half its volume. Save for Groups III, IV, and V.

Precipitate. Contains CuS, Bi₂S₃, CdS, HgS, PbS, SnS₂, Sb₂S₃, and As₂S₃. Add 10 drops (NH₄)₂S soln. (see Notes 19 and 29) and heat on steam bath for 1 min., with stirring. Centrifuge and save filtrate. Repeat treatment of precipitate with hot (NH₄)₂S, centrifuging and combining the filtrate with that from the first treatment. Wash precipitate with NH₄NO₃·H₂S soln. and discard the wash liquid.

Filtrate. Contains members of Group IIB as (NH₄)₃AsS₃, (NH₄)₃-SbS₃ and (NH₄)₃SnS₄. Treat as described under the heading Group II B.

Precipitate. Contains sulfides of Group II A metals. Analyze as described under the heading Group II A.

GROUP II A ANALYSIS

To the precipitate from the subgroup separation, add 10 drops 3N HNO₃ and heat for 3 to 4 min. on steam bath. Filter and wash precipitate with cold water.

Filtrate. Contains any Pb, Cu, Bi and Cd as nitrates. Add 3 drops 6N H₂SO₄ and evaporate to $\frac{1}{4}$ original volume (no smaller). Cool, then add 1 ml. of cold water, and stir. Let stand. Filter and wash ppt. with 50 % alcohol. (See Note 30.)

Filtrate. Cu⁺⁺, Bi⁺⁺⁺ and Cd⁺⁺. Add an excess of conc. NH₄OH. (See Note 32.) *Filter even if no ppt. is visible.* Wash any ppt. with dilute NH₄OH.

Filtrate. Cu and Cd. (See next page.)

Precipitate. Bi(OH)₃. Dissolve in 5 drops 3N HCl. To 1

drop of this solution on watch glass add 1 drop of cinchonine reagent.

ORANGE PPT.
indicates Bi⁺⁺⁺ present.

Confirm again by adding to another portion of the soln. on filter paper 2 drops of fresh sodium stannite soln. (See Note 15.)

BLACK COLORATION
confirms Bi⁺⁺⁺ present.

Precipitate. PbSO₄. Heat almost to boiling with 10 drops saturated NH₄Ac soln. (See Question 11 and page 36.) Filter. To filtrate on black background add 2 drops K₂CrO₄ solution.

YELLOW PPT.
confirms Pb⁺⁺ present.

Precipitate. Contains S and/or HgS. Divide ppt. into two parts. (See Note 31.) Test as follows:

To one portion add aqua regia and evaporate to dryness. Add 2 drops water, stir, and filter. To one drop solution on a watch glass add 1 drop stannous chloride.

WHITE, GRAY, or BLACK PPT.
indicates Hg⁺⁺.

To a second portion of the ppt. add 10 drops bromine water, boil one min., filter. To the filtrate add 2 drops of 6N H₂SO₄ and evaporate until SO₂ fumes appear. Cool, add 3 drops of water and 2 drops of sat. NaAc solution. Then add 2 drops of diphenylcarbazide solution.

DEEP BLUE
indicates Hg⁺⁺ present.

Filtrate from the separation of Cu^{++} and Cd^{++} from Bi^{+++} . This filtrate contains Cu^{++} and Cd^{++} . Divide it into two equal parts. Use one portion for the Cu^{++} tests and the other for the Cd^{++} tests as follows:

For Cu^{++} :

If the solution has a **BLUE COLOR** Cu^{++} is present.

Confirm by testing 1 drop of the solution on a watch glass with 1 drop 6*N* acetic acid and 1 drop $\text{K}_4\text{Fe}(\text{CN})_6$ solution.

RED PPT.

indicates Cu present.

To another drop of the solution on filter paper add 1 drop α -benzoinoxime.

GREEN SPOT

confirms Cu^{++} present.

For Cd^{++} :

To test for cadmium, treat the portion of filtrate saved for that purpose in one of the following ways:

If copper is present:

Add KCN solution, (*Caution:* be sure the solution is strongly ammoniacal before adding KCN), drop by drop until the blue of the copper has disappeared. Add 3 more drops of KCN; then pass in H_2S for 2 to 3 min.

YELLOW PPT.

indicates Cd^{++} present.

(See Note 33.)

Confirm by test described below.

If copper is absent:

See Note 33 and use procedure described there. Or proceed as follows:

Pass H_2S into the solution for 2 to 3 min.

YELLOW PPT.

indicates Cd^{++} present.

Confirm by test described below.

To confirm the presence of Cd^{++} , dissolve the yellow precipitate obtained in the procedure used above, in warm 1:4 H_2SO_4 . Filter. To 1 drop of the filtrate on filter paper add 2 drops 6*N* NaOH and a small crystal of thiosinamine and warm in a steam jet. **YELLOW COLORATION or PPT.** confirms Cd^{++} present.

GROUP II B ANALYSIS

To the filtrate from the sub-group separation add dil. HCl until *faintly acid*. (See Note 35.) Filter. (See Note 36.) Wash precipitate with $\text{NH}_4\text{NO}_3 \cdot \text{H}_2\text{S}$ soln.

| | |
|------------------------------|--|
| Filtrate. Discard. | Precipitate. Sulphides of As, Sb and Sn. Add 10 drops conc. HCl, warm on steam bath and stir for 1 min. Cool and add 2 drops water. Filter. |
|------------------------------|--|

Filtrate. Containing SbCl_3 and SnCl_4 . Divide into four equal parts and test as follows:

Place the first portion in a microbeaker. Add an equal volume of water (*exactly*) and pass in H_2S for 1 min.

ORANGE PPT.

indicates Sb^{+++} present. (See Note 38.)

Take a second portion of the filtrate and add 1N NaHCO_3 soln. to it until it is just weakly acid or until a precipitate starts to form. Redissolve any precipitate by adding 1 drop 6N HCl. Heat the soln. to boiling, remove from flame and quickly add a crystal of sodium thiosulfate about the size of a pea. Let stand about 1 min.

ORANGE PPT. or COLORATION of SbOS_3

Confirms Sb^{+++} present.

To the third portion of filtrate in a microbeaker add one small aluminum filing and warm slightly (see Note 24). If any black precipitate is left after gas evolution ceases, add 2 drops conc. HCl and warm again until *all traces of gas evolution* cease. Filter quickly (using cotton plug if necessary). Cool, and add 1 drop cacotheline soln.

VIOLET SOLN.

indicates Sn present. (See Note 39.)

Precipitate. As_2S_3 (and As_2S_5). Place in a crucible, add 10 drops of aqua regia and evaporate *barely* to dryness. Dissolve the residue in 5 drops water and 1 drop of 6N acetic acid and stir. Use as follows: To 1 drop of the soln. on a spot plate add 2 drops saturated ammonium acetate and 1 drop AgNO_3 soln.

CHOCOLATE PPT.

indicates arsenic present. (See Note 40.)

To the remainder of the solution add 1 drop NaHSO_4 soln. and warm for 1 min. on steam bath. Then add 5 drops 6N NaOH and transfer to a gas evolution tube. Place a drop of AgNO_3 solution on a bit of filter paper and put the latter in the bulb of the gas evolution apparatus. Drop four granules of arsenic-free aluminum filing into the NaOH solution and quickly put top of apparatus in place. Set apparatus aside for about 10 min. (See Note 37.)

YELLOW, BROWN or BLACK STAIN

confirms As present.

Treat the fourth portion of filtrate with an aluminum filing as in previous paragraph. Filter, and add to filtrate 1 drop HgCl_2 soln.

WHITE, GRAY or BLACK PPT.

indicates Sn present.

(very specific if obtained, but less sensitive).

7. Stannous and Stannic Ion, Sn^{++} and Sn^{++++} . *a.* Pass H_2S into 2 drops Sn^{++} test solution until precipitation is complete. Filter and wash precipitate. Divide into two portions.

To one portion of the precipitate add 5 drops $(\text{NH}_4)_2\text{S}$ solution and warm. Acidify the resulting solution with 1N HCl.

To the second portion add 5 drops concentrated HCl and warm until all precipitate dissolves. To 2 drops of this solution on a watch glass add 1 drop HgCl_2 solution. To the remainder of the solution add 1 drop cacotheline solution and note the color change (see Note 23) (6, 56).

b. To 2 drops Sn^{++} test solution add 1 drop 0.1N NaOH solution. Note the precipitate of $\text{Sn}(\text{OH})_2$ that forms. Now add 1N NaOH, drop by drop, until the precipitate just redissolves. The resulting solution is a solution of sodium stannite.

c. Pass H_2S into 2 drops Sn^{++++} test solution. Filter and wash the precipitate. Divide into two parts.

Test the solubility of one part in hot $(\text{NH}_4)_2\text{S}$. Reprecipitate by making the solution *faintly acid*.

Dissolve the remainder in 10 drops concentrated HCl. To this solution add the smallest possible granule of zinc. Heat until all the zinc is dissolved. To the solution add a drop of HgCl_2 solution (see Note 24).

GROUP III METALS

CHEMICAL CHARACTERISTICS*

Iron. Iron is a gray metal, having a melting point of 1535°C ., a boiling point of 3000°C ., and a density of 7.86. It is a moderately active metal, reacting slowly at ordinary temperatures with oxygen, chlorine, and many other non-metals. It reacts rapidly, at high temperatures, with oxygen to form Fe_3O_4 ; with sulfur, to form FeS ; and with

* For other typical reactions that have application to analysis, see Auxiliary Tests.

steam, to form Fe_3O_4 and hydrogen. It dissolves readily in HCl , H_2SO_4 , or dilute HNO_3 . Cold, concentrated (or fuming) HNO_3 , however, changes it to "passive" iron—a form which will not show any of the usual reactions of iron.*

Compounds of Iron. Iron forms ferrous, Fe^{++} , and ferric, Fe^{+++} , ions. The former readily oxidize to the ferric state in the presence of oxygen, bromine, chlorine, and other oxidizing agents. As many of the ferric compounds important in analysis are less soluble than the corresponding ferrous compounds, any ferrous ion is usually oxidized to the ferric state before the analysis is attempted.

Ferrous Compounds. From solutions containing ferrous ions, NH_4OH and alkalis precipitate $\text{Fe}(\text{OH})_2$, white,† insoluble in water or excess alkali; but soluble in high concentrations of ammonium salts and in acids. The $\text{Fe}(\text{OH})_2$ quickly oxidizes to $\text{Fe}(\text{OH})_3$ in the presence of air or other oxidizing agents (such as Na_2O_2).

H_2S or $(\text{NH}_4)_2\text{S}$ precipitates FeS from neutral solutions, or more quickly, from alkaline solutions of ferrous ions. FeS is black, insoluble in water or alkalis but soluble in quite dilute acids.

KCN precipitates yellowish $\text{Fe}(\text{CN})_2$, soluble in excess KCN [to form $\text{Fe}(\text{CN})_6^{4-}$] and in acids.

$\text{K}_3\text{Fe}(\text{CN})_6$ precipitates blue $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$ (Turnbull's blue).

$\text{K}_4\text{Fe}(\text{CN})_6$ precipitates white $\text{Fe}_2\text{Fe}(\text{CN})_6$ [usually tinged blue, owing to air oxidation forming small amounts of Prussian blue, $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$].

* It is believed that the strong HNO_3 forms a thin, unstable film of oxide on the surface of the iron, and that this protects the iron from any reagents that may be applied. This film is destroyed by heating, scratching, or striking the iron sharply.

† As usually precipitated, $\text{Fe}(\text{OH})_2$ has a greenish color. This is due to the fact that it is very difficult to prepare or keep ferrous salts free of ferric compounds. The trace of $\text{Fe}(\text{OH})_3$ that precipitates colors the $\text{Fe}(\text{OH})_2$. It will be found that other ferrous compounds, as ordinarily precipitated, exhibit similar anomalies.

Dimethylglyoxime gives a red coloration which slowly fades, as the Fe^{++} ions are oxidized by air to the ferric state.

Soluble carbonates precipitate FeCO_3 , white at first but turning green on standing; soluble in acids.

Ferric Compounds. NH_4OH and alkalis precipitate $\text{Fe}(\text{OH})_3$, red-brown, less soluble in water than $\text{Fe}(\text{OH})_2$ and insoluble in alkalis or in solutions of ammonium salts; soluble in acids.

H_2S or $(\text{NH}_4)_2\text{S}$ precipitates a mixture of sulfur and FeS , the sulfide first reducing the Fe^{+++} to Fe^{++} .

$\text{K}_3\text{Fe}(\text{CN})_6$ gives a brown coloration with solutions containing Fe^{+++} .

$\text{K}_4\text{Fe}(\text{CN})_6$ gives a dark blue precipitate of $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ (Prussian blue).

KSCN gives a deep red color with solutions containing Fe^{+++} , owing to the formation of the slightly ionized $\text{Fe}(\text{SCN})_3$.*

Soluble carbonates give a precipitate of basic ferric carbonate decomposed, by boiling, into $\text{Fe}(\text{OH})_3$.

Soluble phosphates precipitate brown FePO_4 , soluble in excess reagent (forming complex ions) or in mineral acids.

Acetates precipitate red-brown $\text{Fe}(\text{OH})_2(\text{C}_2\text{H}_3\text{O}_2)$ from hot solutions of Fe^{+++} ions.

Aluminum. Aluminum is a silvery rather soft metal, having a very low density (2.7), a melting point of 648°C ., and a boiling point of 1800°C . It is very active, but due to the formation of a protective film of oxide that quickly forms on its surface, it is not readily attacked by oxygen or moisture. It dissolves readily in HCl , dilute H_2SO_4 , or in solutions of alkalis (forming AlO_2^-) but is unaffected by HNO_3 .†

* The color does not form if fluorides, phosphates, oxalates or tartrates are present, as these form very stable complex ions with the iron. If the cold solution is made acid with nitric acid, however, the test may be used successfully.

† This is generally attributed to the formation of a protective film of oxide, as in the case of iron. However, HCl readily destroys this film.

Compounds of Aluminum. All the salts of aluminum hydrolyze almost completely in neutral solution, precipitating $\text{Al}(\text{OH})_3$.

NH_4OH , $(\text{NH}_4)_2\text{S}$ (or H_2S in NH_4OH solution), alkalis, and carbonates precipitate $\text{Al}(\text{OH})_3$, a white gelatinous precipitate, insoluble in acetic acid but soluble in alkalis (forming AlO_2^-)* or in mineral acids.

Phosphates precipitate AlPO_4 , white, soluble in alkalis or in mineral acids.

Acetates produce no precipitate with cold solutions of Al^{+++} , but on boiling, a white basic acetate, $\text{Al}(\text{OH})_2(\text{C}_2\text{H}_3\text{O}_2)$, is precipitated. This is readily soluble in acids and in alkalis.

Certain dyes, such as aluminon (the ammonium salt of aurin tricarboxylic acid) form characteristic colored "lakes" with $\text{Al}(\text{OH})_3$.

For other characteristic reactions of aluminum, see Auxiliary Tests.

Chromium. Chromium is a silvery, rather brittle metal, having a melting point of 1615°C . and a density of 6.92. It dissolves in HCl , dilute H_2SO_4 , or alkalis but, like aluminum, is not dissolved by nitric acid. It is very similar to aluminum in many respects, but differs in that chromium forms complex ions and forms compounds in which it exhibits many different valences.

Compounds of Chromium. Although chromium forms compounds corresponding to the oxides, CrO , Cr_2O_3 , CrO_2 , and CrO_3 (as well as several less known, higher oxides) the most common are those formed from Cr_2O_3 and CrO_3 . Of these, CrO and Cr_2O_3 are basic anhydrides, though Cr_2O_3 is also somewhat amphoteric. CrO_3 is an acidic oxide, dissolving in water to form chromic acid, H_2CrO_4 . Its normal salts are the chromates; its acid salts are the dichromates.

* For a discussion of the reactions of $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$ and other amphoteric hydroxides see the section on Amphoteric Hydroxides.

The chromous salts (salts of CrO) are strong reducing agents, reacting readily with oxygen and other oxidizing agents to give chromic, Cr^{+++} , ions.

With NH_4OH , $(\text{NH}_4)_2\text{S}$ (or H_2S and NH_4OH), alkalis, and carbonates, chromic salts give a precipitate of $\text{Cr}(\text{OH})_3$, green, slightly soluble in excess NH_4OH (especially if ammonium salts are present) and readily soluble in excess alkali (forming chromite, CrO_2^- , ions) and in acids.

Phosphates give a greenish precipitate of CrPO_4 , soluble in acetic acid and mineral acids.

Acetates produce no precipitate except when considerable quantities of aluminum or iron are present. In this case, chromium coprecipitates with these two metals as the basic acetate.

Alkaline solutions of chromites are oxidized to chromates, $\text{CrO}_4^{=}$, by addition of Na_2O_2 , NaOCl , Br_2 , or Cl_2 . Fusion of chromic compounds with Na_2CO_3 and oxidizing agents (such as Na_2O_2 , KClO_3 , or KNO_3) converts them to Na_2CrO_4 .

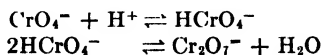
Acid solutions of chromic ion (Cr^{+++}) may be oxidized to dichromate ion ($\text{Cr}_2\text{O}_7^{=}$) by use of strong oxidizing agents such as hot HNO_3 or KClO_3 .

The chromates are strong oxidizing agents, especially in acid solutions. Acids convert them to dichromates.*

Cold concentrated H_2SO_4 gives a red precipitate of CrO_3 with chromates. On heating, the mixture gives off oxygen and the CrO_3 is reduced to a green solution of Cr^{+++} .

If an acid solution of a chromate is treated with H_2O_2 , a green or blue color appears due to the formation of blue perchromic acid, H_3CrO_8 (see Note 46). This rapidly dis-

* The dichromates are acid chromates. The relationship may be shown by the equations for the reaction between H^+ and $\text{CrO}_4^{=}$.



appears as the compound breaks down giving oxygen and Cr^{+++} . It is more stable in ether solutions, however.

If carried out in acetic acid buffered with ammonium acetate, a brown solution is formed, remaining for several minutes.

Many metals form characteristic insoluble chromates. For these, see the discussions on silver, mercury, lead, barium and strontium.

Manganese. Manganese is a gray or reddish-white, very hard, brittle metal having a density of 7.12 and a melting point of 1260°C . It is very similar to iron in activity, combining readily with oxygen, sulfur, chlorine, and many other nonmetals, at high temperatures. Manganese dissolves readily in dilute acids.

Compounds of Manganese. The most important classes of compounds formed by manganese are the pink, manganous, Mn^{++} , compounds; the green manganates, MnO_4^- ; and the violet or purple permanganates, MnO_4^- .

Manganous Compounds. Alkalies and NH_4OH react with solutions of manganous ions to form $\text{Mn}(\text{OH})_2$, white, insoluble in excess alkali but soluble in solutions of ammonium salts and in acids. Air or oxidizing agents quickly convert $\text{Mn}(\text{OH})_2$ to manganous acid, H_2MnO_3 or $\text{MnO}_2 \cdot \text{H}_2\text{O}$.

Soluble cyanides give $\text{Mn}(\text{CN})_2$, brown, soluble in excess of the reagent to form $\text{Mn}(\text{CN})_6^{=}$.

Soluble carbonates precipitate MnCO_3 , white, insoluble in solutions of ammonium salts but readily soluble in dilute acids.

Soluble phosphates precipitate $\text{Mn}_3(\text{PO}_4)_2$, white, soluble in acetic and mineral acids.

$\text{K}_4\text{Fe}(\text{CN})_6$ precipitates $\text{Mn}_2\text{Fe}(\text{CN})_6$, white, insoluble in water but slightly soluble in HCl .

$\text{K}_3\text{Fe}(\text{CN})_6$ precipitates $\text{Mn}_3(\text{Fe}(\text{CN})_6)_2$, brown, insoluble in water and most acids, but somewhat soluble in HCl .

KClO₃ (solid), boiled with concentrated HNO₃ solutions of Mn⁺⁺, gives H₂MnO₃, brown, insoluble in HNO₃.

When manganous compounds are fused with Na₂CO₃ and an oxidizing agent such as air, KClO₃, KNO₃, or Na₂O₂, green Na₂MnO₄ (sodium manganate) is formed. A solution of a manganate will, on acidification, change from green to violet or pink, and a brown precipitate of H₂MnO₃ will settle out. The reaction is



Mn⁺⁺ is oxidized in nitric acid solutions to permanganate, MnO₄⁻, ions by heating with ammonium persulfate, (NH₄)₂S₂O₈, and AgNO₃; with PbO₂, or with KBrO₃. Chlorates or iodates do not act in this way. Sodium bis-muthate gives the reaction in the cold solution, but gives H₂MnO₃, if heated.

The metallic permanganates are all quite soluble. Permanganate ions are oxidizing agents, being reduced in acid solution to Mn⁺⁺, and in alkaline solution to MnO₃⁼.

Zinc. Metallic zinc is a bluish-gray, rather soft metal, having a density of 7.14, a melting point of 419°C., and a boiling point of 907°C. It is quite active, burning readily in air to form white ZnO, and combining with many non-metals (such as chlorine) even at ordinary temperatures. It dissolves readily in dilute acids, or alkalies giving hydrogen.

Compounds of Zinc. Alkalies and NH₄OH react with solutions of Zn⁺⁺ ions precipitating Zn(OH)₂, white and gelatinous, soluble in excess alkali, giving zincate, HZnO₂⁻, ions; in excess NH₄OH or solutions of ammonium salts, giving Zn(NH₃)₄⁺⁺; and in acids.

H₂S or (NH₄)₂S precipitates ZnS from neutral, basic, ammoniacal or acetic acid-sodium acetate solutions, but not from acid solutions (unless the concentration of zinc is

unusually high). ZnS is white, insoluble in water or NH_4OH , but soluble in very dilute mineral acids.

Soluble carbonates precipitate mixed basic carbonates of the type $\text{Zn}_2(\text{OH})_2\text{CO}_3$, white, soluble in NH_4OH or strong solutions of ammonium salts, in alkali carbonates, and in acids. Phosphates precipitate $\text{Zn}_3(\text{PO}_4)_2$, white, soluble in NH_4OH or in acids.

Cyanides precipitate $\text{Zn}(\text{CN})_2$, white, soluble in excess of the reagent to form $\text{Zn}(\text{CN})_4^{=}$. The latter are decomposed by $(\text{NH}_4)_2\text{S}$ to form ZnS .

$\text{K}_4\text{Fe}(\text{CN})_6$ precipitates white $\text{Zn}_2\text{Fe}(\text{CN})_6$.

Cobalt and Nickel.* These elements are both gray metals, nickel being more silvery, in appearance, than is cobalt. Both have a density of 8.9 and a boiling point of 2900°C . The melting point of cobalt is 1480°C . while that of nickel is 1452°C .

Both dissolve readily in HNO_3 ; but while cobalt dissolves readily in dilute HCl and H_2SO_4 , nickel dissolves in them with difficulty.

Both metals readily form a large number of complex ions, and both are capable of existing in either the bivalent state or the trivalent state. In both cases, the most common ions are the bivalent form. However, cobalt is more easily oxidized to form the trivalent ion than is nickel.

Compounds of Nickel. Alkalies precipitate, from solutions of nickelous, Ni^{++} , ions, $\text{Ni}(\text{OH})_2$, green, insoluble in excess alkali but soluble in mixtures of ammonium salts and NH_4OH [forming $\text{Ni}(\text{NH}_3)_4^{++}$] and in acids.

Oxidizing agents such as Br_2 , Cl_2 , or KOCN , oxidize alkaline suspensions of $\text{Ni}(\text{OH})_2$ to black nickelic hydroxide, $\text{Ni}(\text{OH})_3$, insoluble in NH_4OH or KCN .

NH_4OH precipitates a basic salt of the type $\text{Ni}(\text{OH})\text{Cl}$, soluble in the same reagents as is $\text{Ni}(\text{OH})_2$.

* These metals are so similar in nature that it is logical to consider them together in order to bring out their similarities and differences. They are also quite similar to iron.

Carbonates precipitate green NiCO_3 , soluble in mixtures of ammonium salts and NH_4OH , in ammonium carbonate, and in acids.

H_2S or $(\text{NH}_4)_2\text{S}$ precipitate NiS from basic, neutral, or weakly acid (acetic acid-acetate) solutions. NiS is insoluble in $(\text{NH}_4)_2\text{S}$, very slowly soluble in cold 1*N* HCl , but readily soluble in aqua regia or concentrated HNO_3 .

Phosphates precipitate green $\text{Ni}_3(\text{PO}_4)_2$, soluble in dilute acids.

KNO_2 produces no precipitate in dilute solutions of Ni^{++} ions. KCN precipitates green $\text{Ni}(\text{CN})_2$, soluble in excess reagent to form the stable $\text{Ni}(\text{CN})_4^-$. This is decomposed by acids. Solutions of $\text{Ni}(\text{CN})_4^-$ will give NiS with H_2S , but with strong oxidizing agents they decompose giving $\text{Ni}(\text{OH})_3$ and cyanate, CNO^- , ions.

Chromates precipitate a basic chromate from hot, nickelous ion solutions, but react only slowly in the cold.

$\text{K}_4\text{Fe}(\text{CN})_6$ precipitates $\text{Ni}_2\text{Fe}(\text{CN})_6$, green, almost insoluble in dilute HCl .

KSCN gives no visible reaction with nickel solutions.

Compounds of Cobalt. Alkalies or NH_4OH precipitate a blue basic salt of the type $\text{Co}(\text{OH})\text{NO}_3$, insoluble in excess reagent; but soluble in acids, in an excess of KCN , or in strong solutions of ammonium salts. On heating, the basic salt hydrolyzes, forming pink $\text{Co}(\text{OH})_2$. The latter changes to brown $\text{Co}(\text{OH})_3$, slowly, in air, but rapidly if oxidizing agents such as Br_2 , Cl_2 , H_2O_2 , or NaOCl are added.

H_2S or $(\text{NH}_4)_2\text{S}$ precipitates black CoS from neutral or basic solutions. CoS is insoluble in $(\text{NH}_4)_2\text{S}$, and dissolves but slowly in cold dilute (1*N*) HCl . It dissolves readily, however, in hot, concentrated HNO_3 or in aqua regia.

Phosphates precipitate blue-violet $\text{Co}_3(\text{PO}_4)_2$, soluble in NH_4OH .

Carbonates precipitate basic cobalt carbonates, red, soluble in NH_4OH or in ammonium carbonate solution.

KCN precipitates $\text{Co}(\text{CN})_2$, brown, soluble in excess reagent to form very stable cobaltocyanide, $\text{Co}(\text{CN})_6^{4-}$, ions. The latter oxidize readily to cobalticyanide, $\text{Co}(\text{CN})_6^{3-}$, ions.

Chromates precipitate a dark brown basic chromate* from cold solutions of Co^{++} . The precipitate is readily soluble in NH_4OH .

$\text{K}_4\text{Fe}(\text{CN})_6$ precipitates $\text{Co}_2\text{Fe}(\text{CN})_6$, green, almost insoluble in HCl but soluble in NH_4OH .

ANALYTICAL ASPECTS

Group III consists of those metals whose sulfides or hydroxides are precipitated in mildly alkaline solutions of H_2S . To prevent the precipitation of the hydroxides of the fourth group metals and magnesium, it is necessary that the hydroxyl ion concentration, during precipitation of Group III, be kept low, yet constant. For this reason an excess of NH_4OH buffered with ammonium chloride is used to furnish the necessary alkalinity.

On making the solution alkaline, the hydroxides of all the metals of Group III precipitate, with the exception of those of zinc and nickel which remain in solution as ammonia complexes. When H_2S is passed into this solution, the zinc and nickel complexes and the hydroxides of iron, manganese and cobalt are converted into sulfides. The sulfides of aluminum and chromium are peculiar in that, even if they were formed momentarily, they would at once hydrolyze to form the hydroxides again. This is easily understood if one recalls the fact that the sulfides of these metals belong to that class of salts where hydrolysis is most complete, *i.e.*, salts of very weak acids and very weak bases.

The metals of this group are divided into two groups. This division is based on the fact that treating a solution containing these ions with excess alkali will cause the

* One of the separations of cobalt and nickel is based on the fact that cobalt precipitates the basic chromate from cold solutions whereas nickel precipitates very slowly (64).

amphoteric hydroxides of aluminum, chromium and zinc to dissolve while the hydroxides of iron, nickel and cobalt, and the hydrated oxide of manganese, being insoluble in excess alkali, may be filtered off (see page 42).

PRELIMINARY EXPERIMENTS—GROUP III

1. Ferric Ion, Fe^{+++} . On account of the fact that the hydroxides and sulfides of ferric iron are less soluble than those of ferrous iron, it is necessary that all ferrous ions be converted to the ferric state before the analysis of this group begins. This is easily done by adding a few drops of bromine water to the unknown and boiling for a minute. Since this is done first, the reactions that must be considered, are restricted to those of the ferric ion.

a. Pass H_2S into Fe^{+++} test solution for a few seconds (Question 12).

b. To 2 drops Fe^{+++} test solution add 1 drop of a saturated solution of NH_4Cl and 2 drops 6*N* NH_4OH . Saturate with H_2S . Filter and wash the precipitate (see Note 41).

Test the solubility of the FeS precipitate in 6*N* HCl .

c. To 2 drops Fe^{+++} test solution add 1*N* NaOH solution until a copious precipitate forms. Now try to redissolve the precipitate in 6*N* NaOH .

d. To 2 drops Fe^{+++} test solution add, drop by drop, 1*N* NH_4OH until a faint precipitate just appears. Then add 1 drop 1*N* acetic acid and 5 drops 5 per cent ammonium benzoate solution. Dilute to 3 ml. with water; stir, and heat on the steam bath for 5 min. Compare the appearance of the $\text{Fe}(\text{OH})_3$ precipitate with that obtained in part (c) (Note 42). Filter and wash the precipitate with cold water. Dissolve the precipitate in 2 drops 6*N* HCl . Add 2 drops water and test the solution as follows:

To 1 drop of the solution on a watch glass or spot plate add 1 drop $\text{K}_4\text{Fe}(\text{CN})_6$ solution.

To another drop of the solution on a watch glass or spot plate add 1 drop KSCN solution (Question 13).

2. Aluminum Ion, Al^{+++} . *a.* Pass H_2S through 2 drops Al^{+++} test solution for a few seconds.

b. To 2 drops Al^{+++} test solution add 2 drops 6*N* NH_4OH . Now add excess concentrated NH_4OH to the precipitate formed.

c. To 2 drops of Al^{+++} test solution add 1*N* $NaOH$ solution, drop by drop, until a precipitate forms. Then add 6*N* $NaOH$ in excess (Question 14).

To this solution add an equal volume of saturated NH_4Cl solution. Compare the appearance of the precipitate with that of the $Al(OH)_3$ precipitated at first (see Note 43).

d. To 1 drop Al^{+++} test solution add 5 drops water and 3 drops *aluminon* reagent. Now add 1 drop 6*N* NH_4OH , centrifuge, and observe the appearance of the precipitate at the bottom (see Note 44).

e. Repeat (*d*) using alizarin S (blue) instead of *aluminon* (57).

3. Chromic Ion, Cr^{+++} . *a.* Repeat with Cr^{+++} test solution the tests outlined under the headings Aluminum (*a*), (*b*), and (*c*).

b. To 2 drops Cr^{+++} test solution add 6*N* $NaOH$ until the precipitate that first forms redissolves. Now add some Na_2O_2 (about half the size of a grain of rice). (*Caution:* Handle only with a dry spatula as this substance is very corrosive and decomposes when moistened.) Warm on the steam bath for 1 min. then divide the solution into two equal portions (see Note 45).

Acidify one portion with 6*N* HNO_3 . Then make the solution strongly basic with ammonium hydroxide (see Note 46).

To the other portion add 2 drops saturated NH_4Cl and 2 drops $BaCl_2$ solution, stir and filter. Wash the precipitate with cold water twice, then dissolve it in the smallest possible volume of 6*N* HCl . Dilute with 2 drops water and then add a volume of saturated ammonium acetate equal to the total volume of the solution. If no precipitate

appears, scratch the side of the container with a stirring rod for a few seconds (see Note 47).

4. Manganese Ion, Mn^{++} . *a.* Repeat parts (a) and (b) under Ferric Ion using Mn^{++} test solution in place of Fe^{+++} test solution.

b. To 4 drops Mn^{++} test solution add 3 drops 1*N* NaOH solution. Filter and divide the precipitate into four parts.

To one portion of the precipitate add an excess of 6*N* NaOH solution.

To the second portion add 1 drop water and a little Na_2O_2 .

Allow the third portion to stand exposed to air for about 15 min., then compare the results with those obtained with the Na_2O_2 .

Dissolve the fourth portion in 3 drops 6*N* HNO_3 , add 3 drops $AgNO_3$ solution and a little ammonium persulfate, $(NH_4)_2S_2O_8$, about the size of a grain of rice. Heat on the steam bath for 2 to 3 min. Note color of the solution (see Note 48). This test is both sensitive and specific.

5. Zinc Ion, Zn^{++} . *a.* Pass H_2S through 2 drops Zn^{++} test solution for a few seconds.

b. To 2 drops Zn^{++} test solution add 1 drop saturated ammonium acetate solution and saturate with H_2S . Filter and wash the precipitate. Dissolve the precipitate in 1:9 HCl (1 volume concentrated HCl mixed with 9 volumes water). Evaporate the solution to dryness, being careful not to overheat the residue, cool and redissolve in 4 drops water. Divide this solution into two equal parts.

To one part add 1 drop 1:9 HCl, 1 drop 0.1 per cent $CuSO_4$ solution, and 1 drop $HgCl_2 \cdot 4NH_4SCN$ solution. Scratch and let stand if no precipitate appears at first (8, 9, 35). This test is sensitive to 0.05 mg. zinc (see page 67). To the second portion of solution add 1 drop NH_4SCN solution and 1 drop pyridine (26).

c. To 2 drops Zn^{++} test solution add cautiously, drop by drop, 1*N* NaOH solution until a copious precipitate forms. Filter and divide the precipitate into two parts.

To one portion of the precipitate add 1 drop saturated ammonium chloride and 2 drops 6*N* NH_4OH .

To the second portion add 2 drops 6*N* NaOH (Question 16).

6. Cobalt Ion, Co^{++} . *a.* Pass H_2S through 2 drops Co^{++} test solution for a few seconds (Question 17).

b. To 2 drops Co^{++} test solution add 1 drop saturated NH_4Cl solution, 2 drops 6*N* NH_4OH , and saturate with H_2S . Filter and wash the precipitate with $(\text{NH}_4)_2\text{SO}_4$ solution (see Note 49). Divide the precipitate into two equal parts.

Try dissolving one portion in 1:9 HCl (Question 18).

To the second portion add 4 drops aqua regia. Evaporate to dryness, then let the residue cool.

Bend the tip of a platinum wire (a 2-in. wire, sealed into the end of a glass tube which serves as a handle) into a loop

GROUP III ANALYSIS

The unknown may be the filtrate from the precipitation of the sulfides of Group II, or an unknown furnished by the instructor. Add 5 drops bromine water and boil 1 min. Keeping the soln. hot, add 15 drops saturated NH_4Cl soln. and 5 to 6 drops 6*N* NH_4OH . (See Note 52.) Dilute to 4 ml. with water; heat, and saturate with H_2S . Test for completeness of precipitation, adding more H_2S if necessary. (See Note 53.) Filter, and wash precipitate with $\text{NH}_4\text{NO}_3 \cdot \text{H}_2\text{S}$ soln. (See Note 54.)

Filtrate. Acidify at once with HCl and boil to half its volume. Save for Groups IV and V.

Precipitate. Consists of FeS , ZnS , MnS , CoS , NiS , $\text{Al}(\text{OH})_3$, and $\text{Cr}(\text{OH})_3$.

Add 10 drops aqua regia and warm until precipitate dissolves. Neutralize with 6*N* NaOH soln., heat to boiling, and add a few granules Na_2O_2 while stirring. Dilute with 10 drops water, stir, and filter. Wash precipitate with cold water.

Filtrate. Contains AlO_2^- , CrO_4^- , and HZnO_2^- . Analyze as directed under the heading, Group III A.

Precipitate. Consists of $\text{Fe}(\text{OH})_3$, MnO_2 , $\text{Ni}(\text{OH})_3$, and $\text{Co}(\text{OH})_3$. Analyze as directed under the heading, Group III B.

about the diameter of a match stick. Heat this loop to redness in a flame and quickly dip it into a heap of pure borax. Heat the mass of borax that clings to the loop until it fuses into a transparent bead; then, with the bead still hot, dip it into the residue from the aqua regia evapo-

GROUP III A ANALYSIS

To the filtrate from the subgroup separation add 10 drops saturated ammonium acetate soln., stir and heat for 2 min. on the steam bath. Filter and wash the precipitate with cold water. (See Note 55 and p. 42.)

Filtrate. Contains CrO_4^{2-} and HZnO_2^- ions. Use for the following tests:

To one-third of the filtrate add 6N acetic acid with stirring, until the soln. is *faintly* acid to litmus. To 1 drop of this soln. on a white spot plate add 2 drops 50% AgNO_3 soln.

RED-BROWN PPT.

indicates Cr present.

(See Note 58.)

To the other two-thirds of the filtrate add 2 to 3 drops of BaCl_2 . Stir, let stand a minute, then filter.

Filtrate. Contains HZnO_2^- . Acidify with 6N acetic acid and pass H_2S into the soln.

WHITE PPT.

indicates Zn^{++} present.

(See Note 59.)

Precipitate.
A

YELLOW PPT.

confirms Cr present.

Precipitate. $\text{Al}(\text{OH})_3$. Dissolve in 6 drops 2N HCl, and divide into two portions.

To one portion in a centrifuge tube add 3 to 5 drops of *freshly filtered* aluminon reagent, and make *strongly basic* with NH_4OH . (See Note 56.)

RED PPT.

indicates Al^{+++} present.

To the second portion in a centrifuge tube add 3 to 4 drops freshly filtered alizarin S (blue) reagent, and make strongly alkaline with NH_4OH .

BLUE PPT.

confirms Al^{+++} present.

(See Note 57.)

Filter off the precipitate and dissolve it in 6N HCl. Evaporate to dryness, cool and redissolve residue in 5 drops (1:9) HCl. Add to the solution 1 drop 0.1% CuSO_4 soln., 1 drop $\text{HgCl}_2 \cdot 4\text{NH}_4\text{SCN}$ reagent, scratch walls of tube with stirring rod and let stand.

LAVENDER or BLACK PPT.

confirms presence of Zn^{++} .

(See Note 60.)

ration. Heat the bead again until it has become homogeneous, let it cool and look through the bead towards a window or towards a piece of white paper held in a strong white light. The blue color serves as a test for cobalt (see Note 50, and Cobalt under Auxiliary Tests) (33).

c. To 1 drop Co^{++} test solution add 5 drops water, 1 drop Zn^{++} test solution, 1 drop 1:9 HCl solution, and 2 drops

GROUP III B ANALYSIS

Dissolve the precipitate from the subgroup in 6 to 10 drops conc. HNO_3 , warming, if necessary. (See Note 61.) Add 3 to 4 small crystals of KClO_4 and heat for 2 to 3 min. on the air bath, keeping it just below the boiling point. Cool, add an equal volume of water and filter. Wash precipitate with cold water.

Filtrate. Contains Ni^{++} , Fe^{+++} , Co^{++} ions.
Make the soln. strongly basic with NH_4OH , stir, and filter. Wash precipitate with cold water.

Precipitate. $\text{MnO}_2 \cdot \text{H}_2\text{O}$.
DARK BROWN PPT.
indicates Mn present.

Filtrate. Contains Ni^{++} and Co^{++} . Use as follows:

To 1 drop of the filtrate on filter paper add 1 drop dimethylglyoxime soln.

CRIMSON SPOT
shows Ni^{++} present.

To 1 drop of the filtrate on filter paper add 1 drop α -nitroso- β -naphthol, and 1 drop 6N H_2SO_4 .

REDDISH SPOT
indicates Co^{++} present.

To 3 drops of filtrate in a microbeaker add 2 drops 6N HCl, 1 drop Zn^{++} test soln. and 1 drop of $\text{HgCl}_2 \cdot 4\text{NH}_4\text{SCN}$ soln. Scratch walls of beaker and let stand.

BLUE PPT.
confirms Co^{++} present.
(See Note 62.)

Precipitate:

$\text{Fe}(\text{OH})_3$. Dissolve in 6 drops 3N HCl. Divide into two parts.

To one part of the soln. on a spot plate add 1 drop KSCN soln.
RED COLOR
indicates Fe^{+++} present.

To the second part of the soln. add 1 drop $\text{K}_4\text{Fe}(\text{CN})_6$ soln.
DEEP BLUE
confirms Fe^{+++} present.

To half of the precipitate add 5 drops 6N HNO_3 , 1 drop 50% AgNO_3 soln. and a few crystals of ammonium persulfate. Heat for 3 to 4 min.

PINK or VIOLET COLOR
confirms Mn present.

To the other half of the precipitate add 2 drops 6N HCl and warm until it dissolves. Put 1 drop of this soln. on a filter paper, add 1 drop 6N NaOH, and let stand about 2 min. Then add 1 drop benzidine reagent.

BLUE SPOT
confirms Mn present.

$\text{HgCl}_2 \cdot 4\text{NH}_4\text{SCN}$. If no precipitate forms, scratch the side of the beaker for a few seconds* (see Coprecipitation).

d. Place 1 drop Co^{++} test solution on a piece of filter paper and hold the moist spot over a drop of concentrated NH_4OH on a watch glass for a few seconds. To the same spot on the filter paper add 1 drop α -nitroso- β -naphthol solution and 1 drop 6N H_2SO_4 .

7. Nickel Ion, Ni^{++} . a. Repeat tests (a), (b), (c), and (d) as described under the heading Cobalt Ion, using Ni^{++} test solution instead of Co^{++} test solution.

b. Place 1 drop Ni^{++} test solution on a piece of filter paper and hold the moist spot over 1 drop concentrated NH_4OH for a few seconds. Then add 1 drop dimethylglyoxime solution (see Note 51 and Question 19).

GROUP IV METALS

CHEMICAL CHARACTERISTICS

Barium. Barium is a silvery metal, having a density of 3.5, and a melting point of 850°C . It is extremely active, tarnishing quickly in air and reacting readily with most nonmetals. It reacts with cold water giving hydrogen and a precipitate of $\text{Ba}(\text{OH})_2$ and reacts vigorously with dilute acids. As its nitrate and chloride are readily soluble, the best solvent for the metal is very dilute HCl or HNO_3 .

Compounds of Barium. Neither H_2S , $(\text{NH}_4)_2\text{S}$, NH_4OH , nor chlorides cause any precipitation with solutions containing Ba^{++} ions.†

* The authors have found this test to be specific in Group III and more sensitive than the α -nitroso- β -naphthol test. Ferric ion, if present, is removed by addition of microcosmic salt or weakened, after precipitation, by dilution of the red solution.

† BaS , does not precipitate in aqueous solutions by the addition of H_2S owing to the fact that it hydrolyzes and forms the acid salt, $\text{Ba}(\text{HS})_2$, a fairly soluble substance.

As $\text{Ba}(\text{OH})_2$ is moderately soluble, NH_4OH does not furnish a concentration of OH^- sufficiently large to cause its precipitation from any but the most concentrated solutions of Ba^{++} .

Soluble carbonates precipitate BaCO_3 , white, insoluble in NH_4OH or alkalis, but soluble in acetic acid and dilute HCl or HNO_3 .

Alkalies precipitate some $\text{Ba}(\text{OH})_2$ from strong solutions of Ba^{++} . The precipitate is white, insoluble in excess alkali, but soluble in acetic acid, dilute HCl , or HNO_3 .

Phosphates precipitate $\text{Ba}_3(\text{PO}_4)_2$, white, soluble in mineral acids.

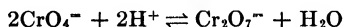
Chromates precipitate BaCrO_4 , yellow, only slightly soluble in strong acetic acid, but soluble in mineral acids.*

Sulfates precipitate BaSO_4 , white, extremely insoluble in water, alkalis, or acids. Slightly soluble in hot concentrated H_2SO_4 .†

Oxalates give a white precipitate of BaC_2O_4 , only slightly soluble in water but soluble in hot dilute acetic acid.

$\text{K}_4\text{Fe}(\text{CN})_6$ gives a white precipitate of $\text{Ba}_2\text{Fe}(\text{CN})_6$ or $\text{BaK}_2\text{Fe}(\text{CN})_6$, depending on the relative amounts of Ba^{++} and reagent present.

* Solutions of chromates contain chromate, CrO_4^{--} , ions in equilibrium with dichromate, $\text{Cr}_2\text{O}_7^{--}$, ions, according to the equation

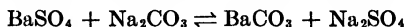


The addition of hydrogen ions favors the formation of dichromate ions, and lowers the concentration of the chromate ions.

Acetic acid, being slightly ionized, does not furnish hydrogen ions in sufficient concentration to repress the chromate ions to the point where BaCrO_4 will dissolve. However, HCl and HNO_3 will do so.

† In order to get the barium in BaSO_4 into solution either of the following procedures may be used:

1. By boiling BaSO_4 with successive portions of strong Na_2CO_3 , a precipitate of BaCO_3 will be left behind. The reaction is:



The BaCO_3 can then be dissolved in acetic acid, HCl , or HNO_3 .

2. Fusion of BaSO_4 with Na_2CO_3 causes the conversion of BaSO_4 to BaCO_3 . The Na_2SO_4 formed is dissolved in water, leaving the insoluble BaCO_3 behind. The BaCO_3 is then dissolved in acetic acid, HCl , or HNO_3 .

3. If a mixture of BaSO_4 , Na_2CO_3 , and powdered charcoal is heated on a charcoal block in the reducing flame of a blowpipe, the BaSO_4 is reduced to BaS . The latter is readily soluble in acids.

BaCl_2 and $\text{Ba}(\text{NO}_3)_2$ are soluble in water but insoluble in absolute alcohol or acetone.

Strontium and Calcium. These metals are very similar to each other and to barium. They are both very active metals reacting with the same reagents and in the same manner as does barium. Calcium is a rather soft metal, being slightly harder than lead. Calcium has a density of 1.55 and a melting point of 810°C . Strontium has a density of 2.6 and a melting point of 752°C . The solvents for these metals are the same as for barium.

Compounds of Strontium and Calcium. With few exceptions, solutions of Ca^{++} or of Sr^{++} give the same type of compounds as would solutions of Ba^{++} . The most notable exceptions are as follows:

Chromates do not give precipitates with neutral or acid solutions of Ca^{++} or Sr^{++} . If the solution is slightly alkaline, however, Sr^{++} gives SrCrO_4 , yellow, readily soluble in acetic acid, HCl , or HNO_3 , but insoluble in alcohol or alcohol-water mixture.

Sulfates precipitate SrSO_4 from solutions containing Sr^{++} , but give no precipitate with Ca^{++} unless the latter are present in very high concentrations.

Oxalates precipitate SrC_2O_4 and CaC_2O_4 , neither of which dissolves readily in acetic acid, but both of which are soluble in mineral acids.

$\text{K}_4\text{Fe}(\text{CN})_6$ gives no precipitate with either Ca^{++} or Sr^{++} . The anhydrous chloride and nitrate of strontium are insoluble in either absolute alcohol or anhydrous acetone. The corresponding salts of calcium, however, are soluble in both of these solvents.

ANALYTICAL ASPECTS

Owing to the facts that the chlorides of barium, strontium, and calcium are very soluble and that their sulfides cannot be precipitated from aqueous solutions, they are not

precipitated with either Group I, II, or III. However, their carbonates are precipitated by addition of ammonium carbonate to an alkaline solution of their ions. Magnesium carbonate is also precipitated under these conditions, but, if the alkalinity of the solution is lowered by addition of a large concentration of an ammonium salt followed by the addition of the ammonium carbonate, magnesium carbonate will not precipitate.

The identification of these elements is based upon (1) the low solubility of their carbonates, (2) the difference in solubility of their chromates (see Note 63), and (3) the low solubility of calcium oxalate, CaC_2O_4 .

PRELIMINARY EXPERIMENTS—GROUP IV

1. Barium Ion, Ba^{++} . *a.* To 2 drops Ba^{++} test solution add 1 drop 3*N* K_2CrO_4 solution. Filter and wash the precipitate twice with cold water. Now add 5 drops 1*N* acetic acid and 5 drops 2.5*N* ammonium acetate solution and stir well. Centrifuge (Question 23).

To some of the filtrate add dilute NH_4OH until faintly basic. Add 10 drops alcohol and stir (Question 24).

b. To 2 drops of the hot test solution add 1 drop saturated ammonium chloride solution and 1 drop ammonium carbonate reagent (see Note 64). Filter and wash precipitate with cold water.

Dissolve the precipitate in 2 drops dilute acetic acid, warming if necessary. Now add 1 drop 3*N* K_2CrO_4 solution, filter, and wash the precipitate once. Make a small loop in the end of a clean platinum wire (see Note 65); dip the loop into the precipitate until a little adheres to the wire. Hold for a few seconds in the fumes from a little concentrated HCl in a microbeaker, then hold in the edge of the hot nonluminous flame of your burner. Note the faint greenish tinge imparted to the flame. This is an excellent confirmatory test for Ba^{++} (see Note 66).

2. Strontium Ion, Sr^{++} . *a.* To 2 drops Sr^{++} test solution add 1 drop saturated NH_4Cl solution, heat, and add 1 drop ammonium carbonate reagent (Question 25). Filter, wash, and add 2 drops dilute acetic acid to the precipitate.

b. To the solution thus obtained add 1 drop $3N$ K_2CrO_4 soln. (Question 26 and Note 67.) Now add 2 drops dilute NH_4OH and 5 drops alcohol. Filter and wash the precipitate once.

c. To the precipitate from (a) add 5 drops $1N$ acetic acid and 5 drops $2.5N$ ammonium acetate solution. Stir (see Question 27 and Note 68). To the solution thus obtained add NH_4OH until it is faintly basic and then add an equal volume of alcohol. Filter and wash precipitate.

d. Using the precipitate from (b), try the flame test as described under Barium Ion *b*. The crimson flame is a confirmation of the presence of strontium.

3. Calcium Ion, Ca^{++} . *a.* Repeat (2a) using Ca^{++} test solution instead of Sr^{++} test solution. Save the solution for (b).

b. To the solution from (a) add 1 drop $3N$ K_2CrO_4 solution and 2 drops dilute NH_4OH . Then add an equal volume of alcohol (Questions 28 and 29). Save the solution for (c).

c. To the clear solution from (b) add 1 drop $3N$ potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4$) solution. Heat and let stand for 15 min. or more (see Note 69). Filter. Wash precipitate and save it for part (d).

d. With the precipitate from part (c) try the flame test as described under Barium Ion *b*. The faint, momentary brick-red tinge imparted to the flame is an excellent confirmation of the presence of Ca^{++} .

e. To 1 drop Ca^{++} test solution add 2 drops water and 1 drop $1N$ K_2SO_4 solution. Scratch the side of the microbeaker and let stand for 5 min. Filter. To the clear filtrate add 1 drop $3N$ potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4$), scratch the walls of the container again, and let stand.

GROUP IV ANALYSIS

Unknown (or filtrate from Group III). Acidify the filtrate from Group III, or the group unknown with 6*N* HCl and evaporate to half its volume. Filter and discard any precipitate. To the filtrate add 6*N* NH₄OH until the soln. is faintly alkaline, heat on the steam bath, and add ammonium carbonate reagent, drop by drop, until precipitation is complete. (See Note 70.) Filter and wash the precipitate twice with cold water.

Filtrate. Save for Group V.

Precipitate. Contains BaCO₃, SrCO₃, and CaCO₃. Dissolve in smallest possible volume of 6*N* acetic acid (see Note 71), warming if necessary. Evaporate just to dryness and cool the residue. Dissolve the residue in 10 drops of 1*N* acetic acid and add 10 drops 2.5*N* ammonium acetate soln. Then add 3*N* K₂CrO₄ soln., drop by drop, until the clear liquid, after stirring and centrifuging, has a distinct yellow color. Add 3 drops 6*N* NH₄OH and more K₂CrO₄ soln. until the filtrate again has a persistent yellow color. Add half its volume of alcohol and stir. Filter, and wash the precipitate with a mixture of 5 drops alcohol, 5 drops water, and 1 drop 6*N* NH₄OH.

Filtrate. Contains CaCrO₄ and possible small amounts of SrCrO₄. Add an equal volume of alcohol and 1 drop 1*N* K₂SO₄ soln. and let stand. Filter off any precipitate that forms, and discard it.

To the clear filtrate add 2 drops 3*N* potassium oxalate, K₂C₂O₄, soln., heat to boiling (see Note 72), and let stand for about 15 min. Centrifuge.

WHITE PPT.

indicates Ca⁺⁺ present.

Confirm by flame test, using the precipitate above as described in Preliminary Experiment 1b.

FAINT BRICK-RED
flame confirms Ca⁺⁺ present.

Precipitate. Contains BaCrO₄ and SrCrO₄. Add 5 drops 1*N* acetic acid and 5 drops 2.5*N* ammonium acetate soln., stir, and let stand for about 3 min. Filter and repeat the treatment of the precipitate. Combine the two filtrates. Wash any precipitate with cold water.

Filtrates. (combined): contains SrCrO₄. Add 3 drops 6*N* NH₄OH and a volume of alcohol equal to that of the total filtrate present. Stir and centrifuge.

YELLOW PPT.
or cloudiness indicates Sr⁺⁺ present.

Confirm by flame test using the precipitate above.

CRIMSON FLAME
confirms Sr⁺⁺ present.

Precipitate. BaCrO₄.
The presence of

YELLOW PPT.
at this point indicates Ba⁺⁺ present.

Confirm by flame test using precipitate above.

GREENISH FLAME
confirms Ba⁺⁺.

GROUP V METALS

CHEMICAL CHARACTERISTICS

Magnesium. Metallic magnesium is a silvery metal, having a density of 1.74, a melting point of $651^{\circ}\text{C}.$, and a boiling point of $1110^{\circ}\text{C}.$ It is quite active, reacting slowly with boiling (but not cold) water to give hydrogen and the rather insoluble magnesium hydroxide $\text{Mg}(\text{OH})_2$. It combines readily with oxygen and, at high temperatures, reacts readily with such nonmetals as the halogens, sulfur, and even nitrogen (the last reaction resulting in the formation of magnesium nitride, Mg_3N_2). The metal dissolves readily in dilute acids forming hydrogen gas and magnesium ions.

Compounds of Magnesium. The compounds of magnesium have properties very similar to those of calcium, for which it is often mistaken in analysis. The chromate, MgCrO_4 ; the ferrocyanide, $\text{Mg}_2\text{Fe}(\text{CN})_6$; the chloride, MgCl_2 ; and the nitrate, $\text{Mg}(\text{NO}_3)_2$, are very soluble in water. The sulfides cannot be precipitated from aqueous solutions as hydrolysis of the sulfide readily occurs.

Phosphates precipitate $\text{Mg}_3(\text{PO}_4)_2$ from neutral or slightly basic solutions of Mg^{++} . From ammoniacal solutions of Mg^{++} , containing a large concentration of ammonium salts, white, crystalline MgNH_4PO_4 precipitates. The latter is soluble in acids.

Arsenates give white $\text{Mg}_3(\text{AsO}_4)_2$ with neutral solutions of Mg^{++} or white, crystalline $\text{MgNH}_4\text{AsO}_4$ with ammoniacal solutions of Mg^{++} , containing ammonium salts.

Oxalates precipitate MgC_2O_4 , white, soluble in acids and in excess alkali oxalates.

Sulfates produce no precipitate, as MgSO_4 is very soluble in water.

Soluble carbonates produce a precipitate of MgCO_3 , white, insoluble in NH_4OH , but soluble in solutions of ammonium salts (even in the presence of NH_4OH) and in acids.

NH_4OH or alkali hydroxides produce a precipitate of $\text{Mg}(\text{OH})_2$, white, gelatinous, insoluble in excess alkali, but soluble in solutions of ammonium salts and in acids.

Potassium, Sodium and Ammonium.* Sodium and potassium are very soft metals, having, when freshly cut, a silvery luster. The former has a density of 0.97, a melting point of 97.5°C ., and a boiling point of 880°C . Potassium has a density of 0.86, a melting point of 62.3°C ., and a boiling point of 760°C . Both are extremely active metals, potassium being slightly the more active. Both tarnish almost instantly in air forming oxides, Na_2O_2 , K_2O_4 , and K_2O ; both react vigorously with water giving the hydroxide and hydrogen; both combine readily with nonmetals, many of them at ordinary temperature. With acids, their reaction is so rapid as to be dangerous. The safest solvent is ethyl alcohol.

Potassium, sodium, and ammonium are monovalent in all their compounds.

Compounds of Potassium, Sodium, and Ammonium. Practically all the compounds of these three ions are soluble to a greater or less extent. The hydroxides, sulfates, chlorides, nitrates, carbonates, phosphates, arsenates, chromates, sulfides, and ferrocyanides are all very soluble. However, NH_4OH is very unstable towards heat, and breaks up giving NH_3 and water. Sodium oxalate is less soluble than the oxalates of the other two ions.

A few of the compounds of sodium, potassium, and ammonium are sufficiently insoluble to allow their use in

* Although ammonium is not an element, the radical NH_4 exhibits certain peculiarities that justify its treatment as a metal. Its base- and salt-forming properties are already familiar to the student. In addition, however, it has the ability to form an amalgam with mercury. This is easily demonstrated by either electrolyzing a strong solution of NH_4Cl , using a pool of mercury as the cathode, or by adding some sodium amalgam (a solution of metallic sodium in mercury) to a saturated solution of NH_4Cl . If either of these operations is carried out at a low temperature, an amalgam of ammonium is formed, the truth of this being demonstrated by allowing the amalgam to warm, and noting the escape of hydrogen and NH_3 gases from the mass.

analysis. As these will be considered under Preliminary Tests and under Auxiliary Tests, no further discussion is necessary here.

ANALYTICAL ASPECTS

The members of this group remain in solution throughout all the previous precipitations. Magnesium readily forms a number of slightly soluble compounds but sodium, potassium, and ammonium ions form very few slightly soluble substances. In view of the fact that ammonium ion is added many times during the analysis, it is necessary to test the original solution for that ion.

Most of the reagents that precipitate potassium, also precipitate ammonium ions. It is therefore necessary to destroy the ammonium ion before testing for potassium. This is done by oxidizing the ammonium ion with aqua regia and igniting the residue to drive off the last traces of ammonium compounds. Since none of the other ions interfere with each other in these tests, it is not necessary to do any separation other than this.

PRELIMINARY EXPERIMENTS—GROUP V

1. Magnesium Ion, Mg^{++} . *a.* To 1 drop Mg^{++} test solution add 1 drop ammonium carbonate solution (without NH_4Cl).

Repeat this test using 1 drop Mg^{++} test solution, 1 drop saturated NH_4Cl solution (see Question 30), and 1 drop ammonium carbonate reagent.

b. To 1 drop Mg^{++} test solution add 1 drop 6*N* NH_4OH . Now try redissolving the precipitate in saturated NH_4Cl solution (see Question 31).

To this solution add 1 drop NaH_2PO_4 solution. Scratch inside wall of microbeaker and let stand a few minutes.

c. To 1 drop Mg^{++} test solution add 1 drop *p*-nitrobenzeneazoresorcinol reagent. Stir and centrifuge. Divide the "lake" or precipitate into two portions (58).

To one portion of the "lake" add 6*N* HCl.

To the second portion of the "lake" add 6*N* NaOH (see Note 73).

2. Potassium Ion, K^+ . *a.* To 1 drop K^+ test solution add 1 drop tartaric acid solution (see Note 74).

b. To 1 drop K^+ test solution add 1 drop *freshly prepared* and filtered sodium cobaltinitrite, $Na_3Co(NO_2)_6$, solution (see Note 75).

Repeat using instead of the pure K^+ ion solution a mixture of K^+ and Ag^+ (59) (see Note 76).

c. To one drop K^+ test solution add 1 drop picric acid solution and let stand.

d. Evaporate 1 drop K^+ test solution to dryness. With a platinum wire try a flame test on the residue, looking at the flame through a piece of blue (cobalt) glass. The flame test is capable of detecting as little as 6×10^{-4} mg. potassium (see Note 77).

Repeat this test once more using a mixture of K^+ test solution and an equal volume of Na^+ test solution.

Repeat this test once more using Na^+ test solution alone (see Note 78 and Question 32). It is possible to detect as little as 3×10^{-6} mg. sodium by this method.

3. Ammonium Ion, NH_4^+ . *a.* Repeat the tests under the heading Potassium Ion, parts *a*, *b*, and *c*, using NH_4^+ test solution instead of K^+ test solution (Question 33).

b. Precipitate some $(NH_4)_2NaCo(NO_2)_6$ by adding 1 drop saturated sodium cobaltinitrite solution to 1 drop NH_4^+ test solution. After precipitation occurs, heat the mixture until the precipitate dissolves. Cool, then add more sodium cobaltinitrite solution.

Repeat the above test, using K^+ in place of NH_4^+ (see Note 79 and Question 34).

c. In the test-tube portion of the gas evolution apparatus put 3 drops NH_4^+ test solution and evaporate just to dryness (see Question 35). Cool, add 2 drops 6*N* NaOH, and put the top of the apparatus in place. In the top tube

place a strip of moist red litmus paper, close the top with a loose plug of cotton, and warm the test tube for a few minutes, observing any change in the color of the litmus.

4. Sodium Ion, Na^+ . *a.* Repeat all tests described under the title Potassium Ion using Na^+ test solution instead of K^+ test solution (see Question 36).

b. To 1 drop Na^+ test solution on a watch glass (using a. black background) add 8 drops zinc uranyl acetate solution. Rub the glass in contact with this mixture with a stirring rod a few seconds and let stand. This test will detect as little as 0.00001 g. sodium. Neither K^+ , NH_4^+ , nor Mg^{++} interferes (60, 61).

GROUP V ANALYSIS

Group unknown (or filtrate from Group IV). Divide into six equal parts and perform the following tests.

To one portion add 1 drop saturated NH_4Cl , 1 drop 3N NH_4OH , and 1 drop NaH_2PO_4 . Rub inside wall of beaker with a stirring rod and let stand 10 minutes.

WHITE PPT.

indicates Mg^{++} present.

To another portion of the unknown made *faintly* acid (see Note 73) add an equal volume of p-nitrobenzeneazoresorcinol reagent. Centrifuge.

BLUE LAKE or PPT.

indicates Mg^{++} is present.

Combine two portions of the unknown and evaporate to dryness. Add 10 drops aqua regia and evaporate again to dryness, using a crucible as the container. Ignite the residue (heat the crucible to redness) until no more white fumes escape (Question 37). Cool, then dissolve the residue in 3 drops water. Use this solution for the following tests.

To 1 drop of this solution on a watch glass add 1 drop of sodium cobaltinitrite solution (see Notes 74 and 75). Let stand.

PALE YELLOW PPT.

indicates K^+ present.

Confirm by heating in a microbeaker until precipitate redissolves, cooling and adding more reagent. Reappearance of the precipitate is excellent confirmation for K^+ ion.

To another drop of the prepared solution apply the flame test using the platinum wire and blue glass.

LAVENDER FLAME visible through BLUE GLASS

confirms presence of K^+ .

(See Note 77.)

Combine two portions of the unknown and evaporate to dryness. Cool and dissolve residue in 3 drops water. Test as follows.

To 1 drop of this solution on a watch glass (black background) add 8 drops zinc uranyl acetate solution. Rub inside of container with a stirring rod and let stand 5 min.

PALE YELLOW PPT.

indicates Na^+ present.

Try the flame test with the remainder of the concentrated solution (see Note 80).

BRIGHT YELLOW LASTING FLAME

confirms presence of Na^+ .

The test for NH_4^+ ion must be made on the *original* general or group unknown before any reagents are added to it. The test is carried out as follows:

Evaporate 3 drops of *original unknown* just to dryness in the gas evolution tube (see Note 81). Cool, then add 2 drops 6*N* NaOH solution to the residue. Quickly place a strip of moist red litmus paper inside of the bulb. Warm gently on the steam bath.

Uniform BLUE COLOR to litmus

indicates NH_4^+ present.

(See Note 82.)

(For additional tests, see Ammonium under Auxiliary Tests.)

AUXILIARY TESTS

Sometimes it happens that, owing to the presence of unusual elements in unknowns or to slight errors in procedure, the final identification tests do not give clear-cut results. In such cases it is often necessary to carry out additional tests in order to confirm or disprove the con-

clusions drawn from the usual tests. A few such tests are given here under the headings of the ions for which they are used. For the sake of brevity, only the essentials of the tests are included; and if any extensive use is to be made of them it is suggested that a study be made of the literature cited here. If the original publications are not available, the abstracts should be used, as the information included in them is sufficient for many purposes.

Silver. 1. Zinc purpurate gives a violet precipitate with solutions containing silver ions (see also Mercury). Instructions for preparing the reagent are given by G. Deniges (1).

2. Diphenylthiocarbazon (dithizon) reagent with silver ion in slightly alkaline solutions gives a fine violet precipitate (see also lead, copper, zinc, cadmium, and cobalt) (2, 16).

Mercury. 1. A drop of solution containing mercurous ion placed on a piece of filter paper and treated with a drop of NaNO_2 solution, gives a dark stain of metallic mercury. Silver interferes, but the colored products of copper, iron, nickel, cobalt, and chromium can be washed off (3).

2. If a drop of a solution containing mercurous ion and a drop of aniline are added to a drop of SnCl_2 solution on filter paper, a black stain of metallic mercury will result (4).

3. A small strip of copper placed in a solution containing either mercurous or mercuric ion will become coated with metallic mercury. To distinguish this from the silvery coating given by other metals below copper in the displacement series, the mercury may be rolled into tiny balls by rubbing with the edge of the thumb nail. If the quantity is too small for this, the copper strip may be heated in a tube made by sealing one end of a 5-in. piece of 3-mm. tubing, and the condensation of mercury in the cooler portions of the tube observed.

4. A solution of zinc purpurate gives (in absence of silver ion) a peach-colored precipitate, with mercuric ion.

The reagent is added to the sodium acetate solution of mercuric ion formed after evaporation of the Hg , HgNH_2Cl , or HgS precipitates with aqua regia (1).

5. Diphenylthiocarbazonone has also been suggested as a reagent for mercury (16).

Lead. 1. A drop of a solution containing lead ions, on filter paper, converted to PbO_2 by treatment with H_2O_2 and NH_4OH and heated in a jet of steam to decompose the unused H_2O_2 , will give a blue spot with a 0.1 per cent solution of tetramethyl-diaminodiphenylmethane in 10 per cent acetic acid. Bismuth does not interfere (5, 6).

2. In an alkaline solution containing KCN , lead ions will give a red-violet coloration with diphenylthiocarbazonone reagent. Under these conditions, silver, copper, cadmium, nickel, zinc, and antimony do not interfere (2, 6).

3. A trace of bismuth, followed by a drop of sodium stannite solution, added to an alkaline solution containing lead ions will produce a dark stain of metallic lead in a short time. The bismuth alone gives the test if added in sufficient quantities, so a blank should be run at the same time (7).

Copper. 1. If, to a faintly acid solution containing copper ions, an excess of zinc ions and a drop of $\text{HgCl}_2 \cdot 4\text{NH}_4\text{SCN}$ solution are added, a colored precipitate will be obtained. The color will range from lavender, for minute traces of copper, to a purple-black, for greater concentrations of copper. If copper is present in greater concentration than zinc, an apple-green precipitate of $\text{CuHg}(\text{SCN})_4$ will form (8, 9).

2. Diphenylthiocarbazonone reagent gives a yellow-brown coloration with copper in neutral, or slightly ammoniacal, solutions. Lead, cadmium, zinc, and nickel do not interfere (2, 11).

3. If a solution of copper ions is sufficiently concentrated, the addition of KI solution will produce free iodine and a white precipitate of cuprous iodide. Many metallic

ions interfere with this test, the reaction serving better as a test for moderate concentrations of iodide ion.

Bismuth. 1. If a solution of BiCl_3 or $\text{Bi}(\text{NO}_3)_3$ is treated with a 1 per cent solution of dimethylglyoxime and made strongly ammoniacal, a voluminous yellow precipitate will form (10). If $\text{Bi}_2(\text{SO}_4)_3$ is used in place of the chloride or nitrate, a white precipitate will result (11).

2. If a drop of a solution containing lead ions on filter paper is treated with a solution containing bismuth ions, a drop of 6*N* NaOH, and a drop or two of sodium stannite solution, a black deposit of metallic lead will form (7). The bismuth acts as a catalyst for the reduction of the lead and this reaction serves as a very sensitive test for bismuth. A blank should be run at the same time, however, as the lead will be reduced, in time, whether bismuth is present or not. Easily reduced ions, such as silver and mercury, interfere.

3. A drop of bismuth ion in 10 per cent HNO_3 on filter paper, treated with a dilute solution of KI, will give a black stain of BiI_3 . The stain should be washed with distilled water to remove iodine set free by ferric or cupric ions. Excess KI converts it to a solution of yellow BiI_4^- ion which soon hydrolyzes to orange BiOI . Mercury interferes (12).

Cadmium. 1. If an ammoniacal solution of cadmium ion containing excess KCN is treated with formaldehyde and boiled, a precipitate of $\text{Cd}(\text{OH})_2$ will form. In the presence of dinitrodiphenylcarbazine, the precipitate will be blue. The precipitate of $\text{Cd}(\text{OH})_2$ may be dissolved in dilute HCl and other confirmatory tests applied (13).

2. If a drop of a solution containing cadmium ion is added to a drop of diphenylcarbazine reagent on filter paper, a reddish-violet coloration will be produced. In the presence of both lead and cadmium, a yellow ring of PbI_2 will be surrounded by the reddish-violet ring due to the cadmium. Copper, bismuth, and many other ions interfere.

The reagent is a saturated solution of diphenylcarbazide in 90 per cent alcohol to which has been added a little KCNS and KI (14).

3. A solution containing cadmium ions, treated with a mixture of solid Na_2CO_3 and charcoal in a test tube, evaporated to dryness, then heated strongly, will give a mirror of cadmium metal edged with brown, in the cooler portions of the test tube. If sulfur is added to the test tube and distilled over the mirror, a layer of CdS will form which will be orange while hot, but yellow when cool (15).

4. Diphenylthiocarbazone (2, 6, 16), a 0.5 per cent solution of 1-(2-quinolyl)-4-allyl thiosemicarbazide in 50 per cent alcohol (17), and $\text{HgCl}_2 \cdot 4\text{NH}_4\text{SCN}$ solution (8) have also been suggested as reagents for cadmium. The latter is very slow to produce a precipitate.

Arsenic. 1. CuSO_4 and KOH solutions added to a solution of As^{+++} will, on heating, give a yellow precipitate which, on longer heating, turns orange or red. The precipitate is Cu_2O , formed by the reducing action of the arsenious ion.

2. The solution of As^{+++++} obtained by evaporating the arsenic sulfide precipitate in Group II with aqua regia and dissolving the residue in 3*N* HNO_3 will give a white crystalline precipitate of $\text{MgNH}_4\text{AsO}_4$ if treated with magnesia mixture [a solution of MgCl_2 and NH_4OH to which has been added enough NH_4Cl to prevent precipitation of $\text{Mg}(\text{OH})_2$] and allowed to stand. The usual precautions against supersaturation must be taken, however.

3. A neutral solution of $\text{AsO}_4^{=}$ will give a chocolate-colored precipitate with AgNO_3 . $\text{AsO}_3^{=}$ gives a white precipitate with the same reagent. Chlorides, iodides, bromides, and many other anions interfere.

The test may be carried out by bringing a drop of a solution of As^{+++++} and AgNO_3 in 6*N* HNO_3 into contact with the edge of a drop 6*N* NH_4OH on a glass slide. At

the interface between the liquids a chocolate-colored precipitate will form.

4. A hot solution of ammonium molybdate (3.6 g. MoO_3 dissolved in 7 ml. concentrated NH_4OH and 15 ml. water, followed by addition of a mixture of 25 ml. concentrated HNO_3 and 53 ml. water with stirring) will give with $\text{AsO}_4^{=}$ a yellow precipitate of ammonium arsenomolybdate, $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$.

Tin. 1. A separation of tin and antimony may be made by adding to the slightly acid solution of the mixture a solution of oxalic acid, passing in H_2S , precipitating and filtering off the antimony as Sb_2S_3 . The filtrate is treated with NH_4OH and calcium chloride solution to precipitate the oxalate ion. The solution is made very weakly acid with HCl , and H_2S is passed into the clear filtrate to give a yellow precipitate of SnS_2 . This test is based on the fact that H_2S will not precipitate SnS_2 in the presence of oxalate ion.

2. A slightly acid solution containing tin and antimony, treated with excess of chlorine water and boiled, will precipitate the antimony as Sb_2O_5 . The clear filtrate will then give a yellow precipitate of SnS_2 on adding H_2S (25).

3. If zinc is added to a strongly acid (HCl) solution of tin ions, a small test tube filled with water held in the reacting mixture for about 5 min. and the bottom of the test tube then held in the nonluminous flame of a burner, a pale blue coloration will be imparted to the flame. Many other metals (*e.g.*, copper and lead) interfere, giving their own characteristic colors. The test is significant only if positive (18, 19).

4. If a drop of a solution containing tin (Sn^{++} or Sn^{++++}) is mixed with a drop of 0.05*N* KI solution and a drop of this mixture is brought into contact with a drop of concentrated H_2SO_4 on a glass slide, a fine yellow precipitate of SnI_2 or SnI_4 will form at the interface between the two liquids, gradually spreading into a broader band. Antimony and arsenic

interfere somewhat, giving iodine and a yellow orange precipitate. This, however, usually appears only as a narrow line at the interface without spreading. Controls should be run in case of doubt (20, 21).

5. A borax bead tinted blue by dipping in strong $\text{Cu}(\text{NO}_3)_2$ solution and heating will give with tin (even in traces, and in any type of compound) a red or reddish-violet bead. The color is best developed by heating in a reducing flame. The bead is colorless while hot, the color appearing rather suddenly while cooling (22).

6. Nitrophenylarsonic acid has also been suggested as a precipitation reagent for stannic ions in dilute acid solution (23). Diphenylthiocarbazone gives reddish colorations with stannous ions (16). Stannous ions added to a dried precipitate of Hg_2Cl_2 on filter paper followed by the addition of a drop of aniline gives a dark spot of metallic mercury (very sensitive) (4).

Antimony. 1. A strongly acid (HCl) solution containing antimony ion treated with a drop of $0.05N$ KNO_2 and heated to decompose excess HNO_2 will give a violet color on addition of a drop of a 0.1 per cent solution of rhodamine B (tetraethylrhodamine) in water. Tungsten and oxidizing agents interfere. As little as 0.0005 mg. antimony can be detected in the presence of 12,400 times as much tin by this test (24).

2. By boiling a slightly acid solution with excess chlorine water, antimony can be precipitated as Sb_2O_5 (separation from tin). The resulting precipitate dissolved in HCl may be tested by any of the usual methods (25).

Iron. 1. Ferrous ion gives a dark blue precipitate of ferrous ferricyanide with freshly prepared $\text{K}_3\text{Fe}(\text{CN})_6$ solution. Ferric ion gives only a light brownish solution with this reagent.

2. A solution containing ferrous ions gives a light red precipitate with dimethylglyoxime. Nickel interferes.

3. Solutions containing ferric ions give a red-brown precipitate of basic ferric acetate on boiling with acetate acid mixture.

Aluminum. 1. A drop of a solution of aluminum ion containing a trace of cobalt on a filter paper which was previously treated with saturated KClO_3 solution and dried will, on treatment with NH_3 fumes and burning, leave an ash that varies in color from an olive green to a light blue. In the absence of aluminum ion, the ash is black.

2. If solutions of ammonium chloride and KCNO are added to a solution containing aluminum ions and the mixture is heated, a granular precipitate of $\text{Al}(\text{OH})_3$ will form. Prolonged heating reduces the effectiveness of this precipitation (26).

Chromium. 1. A solution containing $\text{CrO}_4^{=}$ gives a blue coloration with benzidine reagent. The test may be used on a HCl extract from the precipitate of BaCrO_4 (27). The test is not very satisfactory, however.

2. Orcin (*s*-dihydroxytoluene) gives a brown stain with $\text{CrO}_4^{=}$ and strong HCl (6). A 1 per cent solution of strychnine in concentrated H_2SO_4 added to a solution of $\text{CrO}_4^{=}$ gives a blue-violet color, slowly turning red. Manganese, cobalt, $\text{Fe}(\text{CN})_6^{=}$, and oxidizing agents interfere (28).

3. Tetramethyldiamino-diphenylmethane gives a bluish-purple coloration if added to a buffered acetic acid solution of chromate ion. To test for chromic ions, it is best to add the reagent (a 0.1 per cent solution in 10 per cent acetic acid) to the solution, make the latter alkaline with NaOH , and add a few grains of Na_2O_2 . Warm on the steam bath until bubbling has practically ceased, cool, and make acid with acetic acid. A bluish-violet color appears becoming more intense and more reddish on standing. Carried out in this manner on a portion of the filtrate from the aluminum test (see Group III Procedure), this serves as an unusually certain, moderately sensitive test for chromium.

In very dilute solutions the test is faint and fleeting, especially if too great excess of Na_2O_2 is used.

Zinc. 1. Diphenylthiocarbazone forms with zinc ions a red-purple precipitate soluble in the chloroform of the reagent solution. The change is startling, the color going from the rich green of the reagent to a pink or red. Moderate quantities of manganese, cobalt and nickel will not interfere if the solution is made strongly ammoniacal and allowed to stand for a minute or two before adding the reagent. Interference by silver, copper, mercury, gold, bismuth, cadmium, and lead is masked by a preliminary treatment of the solution with $\text{Na}_2\text{S}_2\text{O}_3$. With $\text{Na}_2\text{S}_2\text{O}_3$ and KCN (in *faintly acid* solution to mask nickel, cobalt, and palladium) the reagent is specific for zinc (2, 29).

2. A test developed by Benedetti-Pichler makes use of ashless filter paper soaked in a solution of 4 g. $\text{K}_3\text{Co}(\text{CN})_6$ and 1 g. KClO_3 per 100 ml. water and carefully dried. A drop of zinc solution in the center of a 1-in. square of such paper, dried to a brown spot and burned, will leave a green ash if zinc is present to a concentration of 1 mg. per milliliter. Special methods of using this test will detect as little as 0.0006 mg. of zinc. The ash is best observed if caught on white porcelain (30).

3. A solution containing zinc ions will give a white precipitate if treated with pyridine and solutions of KCNO . The test is less sensitive, however, than the test with pyridine and NH_4CNS (see Group III) (26).

4. Jeffreys and Swift (31) have shown that zinc may be precipitated as the sulfide by passing H_2S into a sulfate-hydrosulfate buffer solution, the hydrogen ion concentration of which may be as high as 2.5×10^{-2} mol per liter. In this manner zinc may be separated from nickel, iron, manganese, chromium, and aluminum. Cobalt, however, comes down with the zinc.

Cobalt. 1. A cold, strongly ammoniacal solution of cobalt will give, with solid $\text{Na}_2\text{S}_2\text{O}_4$ (sodium hyposulfite), a

yellow solution which gradually changes to orange, red, dark brown, and finally forms a black precipitate. Other metals form a brownish-red tint with the solid $\text{Na}_2\text{S}_2\text{O}_4$. On filtering the mixture, however, an orange filtrate is obtained whose color deepens on addition of more reagent (32).

2. If a solution containing cobalt ions is saturated with KCl, treated with a drop of KNO_2 solution, acidified with acetic acid and warmed, a fine yellow precipitate of $\text{K}_3\text{Co}(\text{NO}_2)_6$ will form. The solutions must be stirred with scratching and allowed to stand awhile, as the salt supersaturates readily.

3. Diphenylthiocarbazone may be used in Group III as a specific test for cobalt if the solution is first made alkaline with 2 per cent NaOH. A bluish-violet color first appears, soon fading to a colorless gray (2).

4. The borax bead test described in the preliminary tests on Group III serves as an excellent test for cobalt, giving, according to Curtman and Rothberg (33), a blue bead in a mixture of as high as 95 per cent nickel with 5 per cent cobalt.

Nickel. 1. If, to a neutral or slightly alkaline solution containing nickel ions, a little ethylenediamine and $\text{Na}_2\text{S}_2\text{O}_3$ are added, a violet crystalline precipitate will form. Although this test is not so sensitive as the test using dimethylglyoxime, it is specific in the presence of large concentrations of iron, cobalt, copper, and chromium (34).

2. In the absence of cobalt, the borax bead test (see Preliminary Experiments) gives a reddish-brown color if used on the nickel filtrate in Group III.

Manganese. 1. A solution of manganese ions in concentrated nitric acid gives, on boiling with solid PbO_2 , a pink or violet solution of HMnO_4 (very specific).

2. A drop of a solution of manganese ions made alkaline with NaOH and evaporated to dryness will, on treatment

with a 1 per cent solution of strychnine in concentrated H_2SO_4 , give a blue-violet color, slowly turning red (28). Cobalt interferes, but its interference is removed by preliminary treatment with KCN. Oxidizing agents interfere.

3. A sodium carbonate bead treated with manganese ions, touched while hot to a small crystal of KClO_3 and fused, will give a green bead owing to the formation of sodium manganate (Na_2MnO_4).

Calcium. 1. Calcium may be separated from barium and strontium by converting them to the nitrates, heating strongly to form the anhydrous salt, and treating with anhydrous acetone or absolute alcohol. Calcium nitrate is soluble in these liquids, whereas the nitrates of barium and strontium are insoluble.

Sodium. 1. A neutral solution containing sodium ions will give a white precipitate of $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ if treated with a saturated alkaline solution of potassium pyroantimoniate ($\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$) and allowed to stand. Neither potassium nor ammonium ion will give this test.

2. A solution containing sodium ions will give a yellow precipitate of $\text{NaCo}(\text{UO}_2)_3 \cdot (\text{C}_2\text{H}_3\text{O}_2)_9$ if treated with a solution made by mixing equal volumes of a 4 per cent solution of uranium acetate in 3 per cent acetic acid and a 20 per cent solution of cobalt acetate in 3 per cent acetic acid. The reagent should be allowed to stand over night and should be filtered before using (36).

Potassium. 1. A saturated solution of picric acid in water gives a yellow precipitate with solutions containing potassium ions. Ammonium ion interferes and must be destroyed before the test is applied.

2. Strong perchloric acid added to solutions containing potassium ions produces a white precipitate of KClO_4 . Ammonium ions interfere. Chloroplatinic acid will precipitate potassium as yellow potassium chloroplatinate, K_2PtCl_6 . Ammonium ions give a precipitate of the same appearance, but on igniting, then dissolving the residue in

water and adding more reagent, the ammonium gives no precipitate, while the potassium does.

3. A solution of tartaric acid reacts with neutral solutions of potassium ion to produce a precipitate of $\text{KHC}_4\text{H}_4\text{O}_6$. Ammonium ion produces a similar precipitate of $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$.

4. A 0.1*N* solution of 5-nitrobarbituric acid gives a precipitate with as little as 0.09 mg. of potassium per milliliter. All other ions of Groups IV and V interfere. However, to give the same amount of precipitate requires one hundred times as much sodium as potassium (40).

Ammonium. 1. The tests described under the title Potassium may be used for ammonium ions in the absence of the former. The best way to use them is to make the solution alkaline with NaOH and distill, immersing the delivery tube in a drop or two of distilled water containing a little HCl. As NH_3 is readily volatile, it will distill over and the tests can be applied to the resulting solution. An alternative is to hold a drop of the reagent in the tip of a glass tube over the solution made alkaline with NaOH and to warm the latter, observing the appearance of cloudiness in the reagent.

2. Nessler's solution, an alkaline solution of K_2HgI_4 , turns brownish if added to solutions containing ammonium ions. The depth of color is proportional to the concentration of ammonium ions.

Magnesium. 1. An ammoniacal solution of magnesium ions buffered with NH_4Cl will give a greenish-yellow precipitate on addition of 8-hydroxyquinoline (Oxine) (37, 38). No members of Group V interfere, but several other metals give precipitates of various kinds.

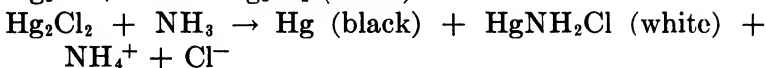
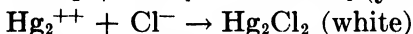
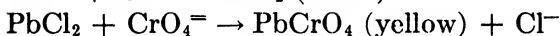
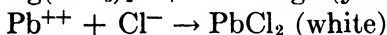
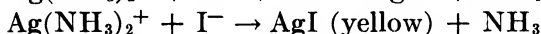
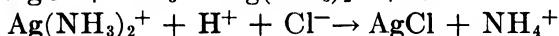
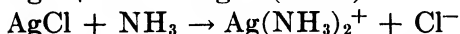
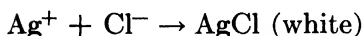
2. An ammoniacal solution of magnesium ions free of ammonium salts, placed on a piece of filter paper and warmed to drive off all ammonia, will, on treatment with phenolphthalein, give a red spot. This will disappear on drying and reappear on moistening (39).

3. Sodium or ammonium carbonate will, in absence of ammonium salts, precipitate MgCO_3 , soluble in excess of saturated ammonium chloride solution.

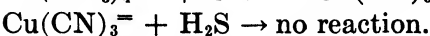
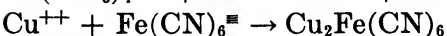
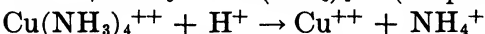
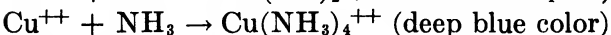
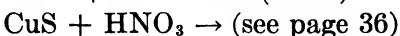
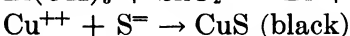
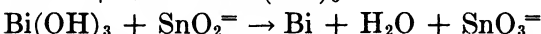
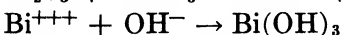
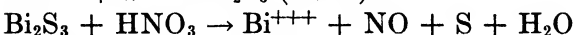
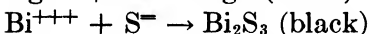
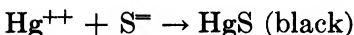
REACTIONS INVOLVED IN SEPARATIONS

[The student should balance each of these for practice, indicating precipitates by (↓) and gases by (↑).]

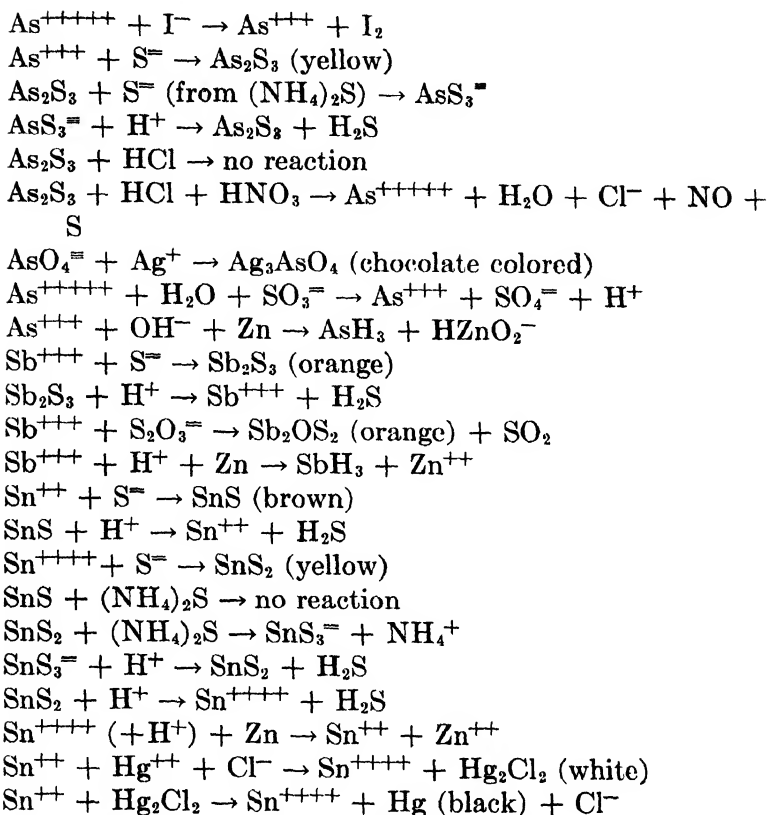
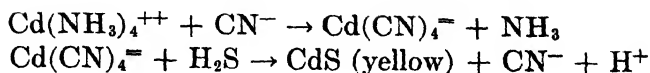
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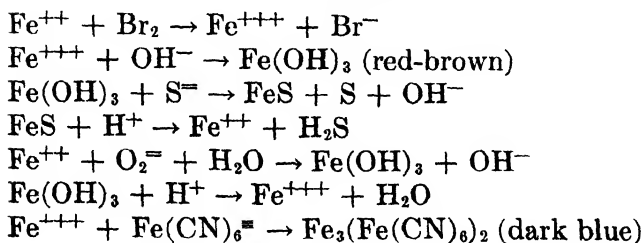
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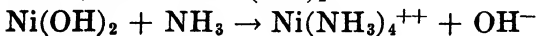
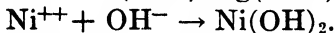
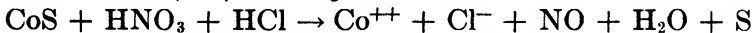
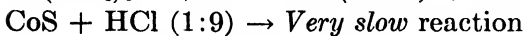
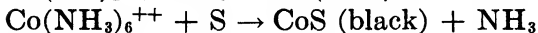
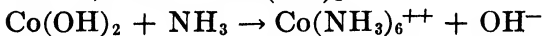
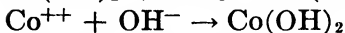
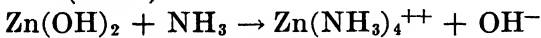
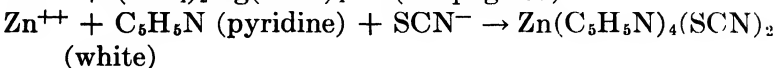
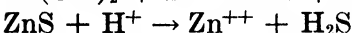
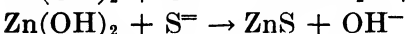
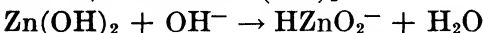
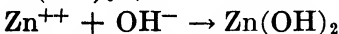
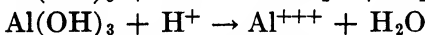
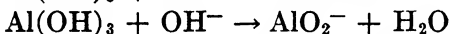
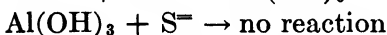
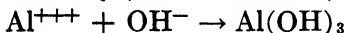
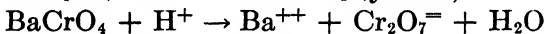
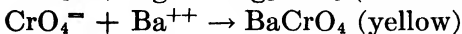
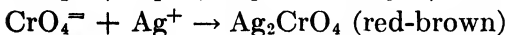
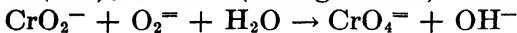
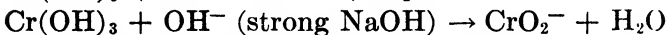
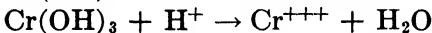
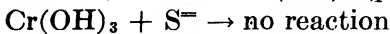
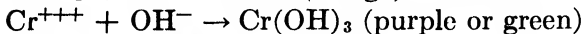
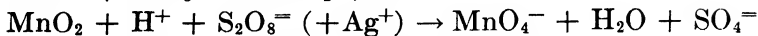
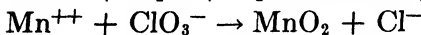
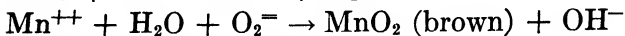
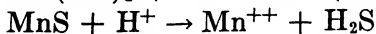
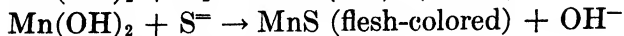
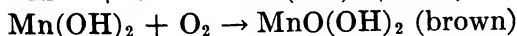
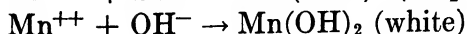
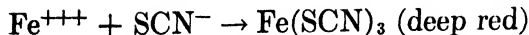


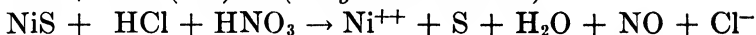
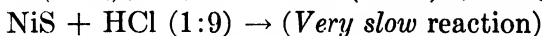
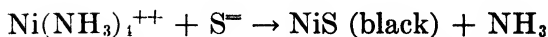
Cd^{++} —all reactions are similar to those of copper except the following:



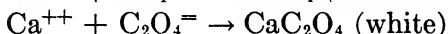
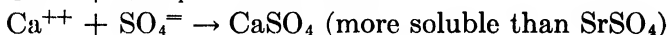
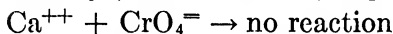
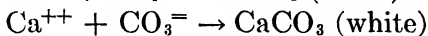
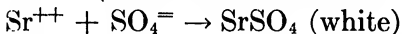
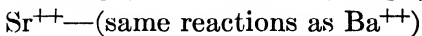
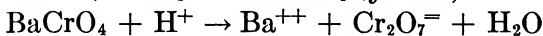
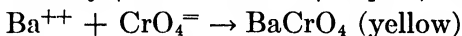
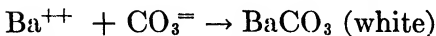
GROUP III



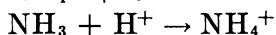
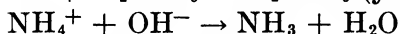
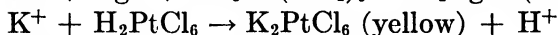
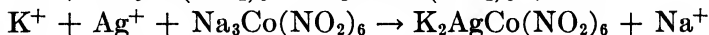
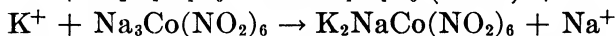
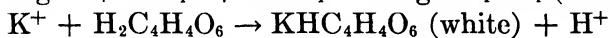
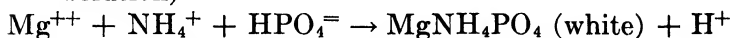
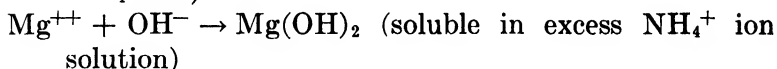
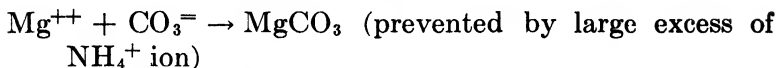




GROUP IV



GROUP V



(Other reactions similar to those of potassium.)

QUESTIONS

1. Does a color reaction seem to show up best as a spot test or as an ordinary beaker precipitation reaction?
2. How could you separate lead chloride from silver chloride?
3. In view of the fact that mercuric acetate, $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$, is a very weak electrolyte show by ionic equations why HgCl_2 should dissolve readily in concentrated solutions of sodium acetate.
4. Is 3N HNO_3 a practical solvent for HgS ?
5. Why is it best to prepare *fresh* aqua regia each time when it is needed as a solvent?
6. Comparing the results obtained from the addition of KI solution to solutions of Hg_2^{++} and Hg^{++} , how could you distinguish between these two ions?
7. How do these results compare with similar tests on Hg_2^{++} ?
8. Is CuS soluble in $(\text{NH}_4)_2\text{S}$? HgS , CdS and Bi_2S_3 act similarly.
9. Why is NH_4OH used so much more than, for example, NaOH (two reasons)?
10. Why is it necessary to add the NH_4I ?
11. By means of ionic equations, show why lead sulfate dissolves in saturated ammonium acetate solution. In terms of solubility products explain why lead chromate precipitates from this solution though lead sulfate does not.
12. Will FeS precipitate when H_2S is added to a neutral solution of Fe^{++} ? Explain in terms of solubility product theory.
13. What background is best for a spot test for the following ions:
 - a. Pb^{++} using K_2CrO_4 solution as the reagent?
 - b. Fe^{+++} using KSCN as the reagent?
 - c. Fe^{+++} using $\text{K}_4\text{Fe}(\text{CN})_6$ solution as the reagent?
14. Does this reaction suggest a way to separate Fe^{+++} from Al^{+++} ? Explain.
15. For what two purposes is ammonium acetate usually used? For what purpose is it used here?
16. Does this suggest a method of separating Zn^{++} from Mn^{++} ? Explain.
17. Does it seem possible to precipitate any of the members of Group III by passing H_2S into a neutral solution of the metallic ion?
18. CoS is soluble in 1:9 HCl . How do you explain its apparent lack of solubility here? How could this be used to separate ZnS from CoS ?
19. Does this test for nickel seem to be very sensitive, i.e., capable of detecting very low concentrations of nickel?
20. By ionic equations and a few words explain the action of ammonium benzoate here. Why is the solution diluted? Why is it heated (see page 27).

21. What is the action of the NH_4Cl here? Explain by ionic equations why it causes the aluminum hydroxide to precipitate. (HINT: See Note 42.)
22. What is the function of the ammonium sulfate in the wash water? (HINT: See Note 49.)
23. Does any of the precipitate seem to have gone into solution?
24. From this (and from your answer to Question 23) would you say that BaCrO_4 is soluble in the buffered solution of acetic acid used?
25. How do these results compare with those from similar treatment of a solution of Ba^{++} ? Of Ca^{++} (see Calcium ion Tests)?
26. Does a precipitate form readily? How does this compare with the precipitation of BaCrO_4 from a similar acid solution?
27. How do your results compare with those obtained for barium? How could you separate BaCrO_4 and SrCrO_4 ?
28. What is the function of the alcohol in these tests?
29. What can you say, from your results, as to the relative solubility of these three chromates? Is this in accordance with what you would expect from a comparison of their solubility products?
30. Explain the results obtained in this experiment.
31. What is the function of the ammonium chloride in this experiment? Explain in terms of the solubility product principle and by means of ionic equations.
32. Do these three tests suggest to you any means of detecting potassium in the presence of sodium, by flame test?
33. Could you distinguish between potassium ions and ammonium ions by means of any of these tests? Give your reasons.
34. How could you distinguish between potassium ions and ammonium ions?
35. Can you suggest any reason why overheating at this point might ruin the test for ammonium ions?
36. Will sodium interfere with the tests for potassium ions? Give your reasons. Could you use the flame test to identify sodium in the presence of potassium ions?
37. What is the purpose of this treatment with aqua regia and ignition? How does the aqua regia act here?

PART IV

ANALYTICAL PROCEDURE—ANIONS

In the analysis of solutions for their metallic constituents, the separations and identifications have been based on the use of solutions of certain anions as reagents. Conversely, the analysis of anions is carried out by making use of their characteristic reactions with cations, such as H^+ ions and certain metallic ions. The laws and rules that apply to cation analysis apply similarly to anion analysis; and it should be easy for the student, with the knowledge gained up to this time, to apply the technique learned earlier, to anion analysis.

As in cation analysis, the anions are divided into groups. Group I consists of those anions which form volatile compounds when treated with HCl ; Group II, those anions which form compounds with $AgNO_3$ which are insoluble in dilute nitric acid; Group III, those anions the calcium or barium salts of which are insoluble; and Group IV, those anions which do not form either volatile compounds with dilute HCl or insoluble compounds with barium, calcium or silver.

PRELIMINARY TREATMENT OF SOLIDS

As in the case of the cation analysis, most of the tests are performed on solutions of the unknown. For this reason, it is necessary to know how to dissolve any solid unknowns that may be issued.

A study of the procedure used in anion analysis makes it obvious that the procedure used in dissolving samples, in preparation for the cation analysis, cannot be used here for any but a few of the anions. For example, the treatment with acids would result in the loss of the members of Anion Group I, as volatile substances. Also, the use of HNO_3 , HCl , and Na_2CO_3 would add NO_3^- , Cl^- , and $CO_3^{=}$ to the solution, and make it difficult to tell whether or not these

ions were present in the original unknown. Addition of some anions cannot be avoided, but it is possible to use the different solvents in places where this causes no trouble. For this reason, it is best to prepare the solid unknown, using a special procedure for each group.

The best and simplest procedure is as follows:

1. Anion Group I. The tests for the members of Group I may be performed, in most cases, on the solid unknown. Thus, where the procedure calls for 1 to 2 drops of a solution of the unknown, a portion of the pulverized solid about the size of a grain of rice may be used.

This procedure is adequate for the detection of the carbonates, sulfites, thiosulfates, nitrites, cyanides, and some sulfides. However, the sulfides of a few metals are insoluble in the HCl used (see Group II Metals), and the sulfide test may be missed if the sulfur is combined with these metals. In case negative results are obtained when testing for sulfides using the solid, heat a sample of the solid unknown (about the size of a match head) for 10 to 15 min. with a strong solution of Na_2CO_3 , and filter. The sulfide test should then be repeated on both the solid residue (if any) and on the filtrate.*

2. Anion Group II. For this, use a sample about the size of an ordinary match head. To prepare the sample for the Group II analysis, first dissolve as much of it in hot water as is possible. Filter, and save the filtrate.

Heat the residue, on the steam bath, with saturated Na_2CO_3 solution for 10 to 15 min. Filter, discarding the precipitate.

Combine the aqueous and Na_2CO_3 filtrates and acidify with dilute H_2SO_4 .† Filter, if any precipitate forms, and use the filtrate for the Group II tests.

* Many of the insoluble sulfides will react, to some extent, with strong, hot solutions of Na_2CO_3 , forming the metallic carbonate and some Na_2S . The latter is soluble in water and reacts readily with dilute HCl.

† Add the acid cautiously as otherwise the CO_2 given off on acidifying the Na_2CO_3 will cause the solution to overflow the sides of the container.

3. Anion Group III. Treat a small sample of the solid unknown with hot water, then with saturated Na_2CO_3 solution, as described in the preparation for Anion Group II.* To the precipitate from the Na_2CO_3 treatment add 6*N* HNO_3 . Heat for 2 to 3 min. on the steam bath, then filter, saving the filtrate. Repeat this treatment, using concentrated HNO_3 this time. Filter, and discard any residue. Finally, combine the filtrates from the treatments with water, Na_2CO_3 , 6*N* HNO_3 , and concentrated HNO_3 . Be sure the solution is acid, then add AgNO_3 until precipitation of Group II anions is complete. Filter, discarding precipitate. Evaporate the filtrate to half its volume. Cool, and neutralize with 1*N* NaOH until the solution is just *faintly acid* to litmus. Use this solution in the tests for $\text{CrO}_4^{=}$, F^- , $\text{C}_4\text{H}_4\text{O}_6^{=}$, $\text{AsO}_3^{=}$, $\text{AsO}_4^{=}$, $\text{PO}_4^{=}$, and $\text{B}_4\text{O}_7^{=}$.

4. Anion Group IV. Since the anions in this group form soluble salts with all the common metals, those compounds in the unknown that contain the members of this group should be soluble in water. Therefore, treat the solid sample with water, heat for 2 to 3 min., and filter. Treat the filtrate in the manner described under the heading Preliminary Treatment of Solutions, Anion Group IV.

PRELIMINARY TREATMENT OF SOLUTIONS

As in cation analysis, the members of one group of anions may interfere with the tests for those of another group. For this reason it is necessary to remove interfering ions before starting the analysis. Since the different groups need slightly different treatment, the procedure used in each

* The combined water and Na_2CO_3 filtrates should be acidified with dilute HNO_3 , filtered (the precipitate being discarded), and a portion of the filtrate saved to use in testing for $\text{SO}_4^{=}$. Otherwise, if the unknown contains Ba^{++} , Sr^{++} , or Pb^{++} , a precipitate of the sulfates will form when the solutions are combined, later. This might result in missing the sulfate test entirely.

Lead, barium, and strontium, if present, remain in the residue from the Na_2CO_3 treatment as carbonates. Later, however, they will be dissolved in acid; and on combining filtrates, the sulfates would precipitate.

case will be discussed under the name of that group for which the final solution is to be used (see Note 84).

1. Anion Group I. For the members of this group, no preliminary treatment is necessary, as the tests are carried out on the vapors escaping from the hot, acid solution.

2. Anion Group II. As the members of Groups III and IV do not interfere with the tests for this group, only Group I need be removed. To do this acidify 1 ml. of the solution with 6N H_2SO_4 and heat on the steam bath for about 5 min. Cool, filter, and use the filtrate to test for the anions in Group II.

3. Anion Group III. Acidify 1 ml. of the unknown solution with 6N HNO_3 , heat just to boiling, and keep the solution hot on the steam bath for 4 to 5 min. Then add AgNO_3 solution, drop by drop, until precipitation is complete.* Filter, discarding the precipitate, and use the filtrate in testing for the members of Group III.

4. Anion Group IV. Acidify 1 ml. of the unknown with dilute H_2SO_4 and evaporate to two-thirds its original volume. Make the filtrate *faintly* basic with NaOH , and add $\text{BaCl}_2 \cdot \text{CaCl}_2$ reagent until precipitation is complete.† Acidify, add AgNO_3 until precipitation is complete, and filter, discarding the precipitate. Filter, and again discard the precipitate. Use the filtrate in testing for ClO_3^- and $\text{C}_2\text{H}_3\text{O}_2^-$. For the nitrate test, prepare as before, only use a saturated solution of Ag_2SO_4 or a little solid Ag_2CO_3 instead of AgNO_3 in removing the anions of Group II.

GROUP ANALYSIS

The analysis of these solutions will be much simplified if the student keeps in mind the characteristics of the various

* The treatment with AgNO_3 is unnecessary if the analysis has shown that the anions in Group II are absent.

† The acidification and evaporation remove members of Group I; the AgNO_3 precipitates the members of Group II; and the $\text{BaCl}_2 \cdot \text{CaCl}_2$ reagent in basic solution removes the members of Group III. If any one of these groups has been shown by analysis to be absent, the procedure for removing members of that particular group may be omitted.

ions that may be in the solution. For example, strong oxidizing ions, such as MnO_4^- , would never be found in solution with strong reducing ions, such as $\text{SO}_3^{=}$, $\text{S}^{=}$, NO_2^- , or I^- , especially if the solution were acid. Similarly, acid solutions will never contain both $\text{S}^{=}$ and $\text{SO}_3^{=}$, for these react, in acid, to form free sulfur and water.

GROUP I ANIONS

This group may contain NO_2^- , $\text{S}^{=}$, $\text{SO}_3^{=}$, $\text{S}_2\text{O}_3^{=}$, $\text{CO}_3^{=}$, or CN^- . Using the solution prepared as described for this group under Preliminary Treatment, perform the following tests:

1. Nitrite Ions, NO_2^- . *a.* In the gas evolution apparatus place 3 drops of the prepared solution. Moisten with dilute H_2SO_4 , and put the top of the apparatus in place. In the testing chamber place a strip of moist starch-iodide paper. Warm the solution and note the color of both vapors and the starch-iodide paper.

Yellow or Brown Gas Giving a Blue Coloration

on the starch-iodide paper indicates that NO_2^- are present.

b. To 2 drops of the solution add 1 drop 0.1*N* ferrous ammonium sulfate and acidify with 6*N* H_2SO_4 . Warm and test vapors as before. If NO_2^- are present, the results will be the same as in (*a*).

2. Sulfide Ions, $\text{S}^{=}$. *a.* In the gas evolution apparatus, place 2 drops of the prepared solution and acidify with dilute HCl . Test the gases in the usual manner with a piece of filter paper moistened with lead acetate solution, warming, if the test is not obtained at first.

Brown or Black Stain

on the filter paper shows $\text{S}^{=}$ are present.

3. Sulfite, $\text{SO}_3^{=}$ and Thiosulfate, $\text{S}_2\text{O}_3^{=}$ Ions (see Note 85). *a.* Place 2 drops of the prepared solution in the gas evolution apparatus and acidify with dilute HCl . Use a

piece of filter paper moistened with a mixture of 1 drop 0.05 per cent KMnO_4 and 1 drop 6N H_2SO_4 , as test paper. If nothing occurs, warm the solution.

Bleaching of Spot

indicates either $\text{SO}_3^{=}$ or $\text{S}_2\text{O}_3^{=}$ present (see Note 86). If, on warming the solution and letting it stand, a yellow precipitate of sulfur forms, $\text{S}_2\text{O}_3^{=}$ may be considered present (see Note 87).

b. To one drop of the prepared solution add 1 drop of 50% AgNO_3 solution and warm almost to boiling.

Yellow or Orange PPT.

turning very **Dark Brown** on standing or heating, indicates $\text{S}_2\text{O}_3^{=}$ present (see Notes 88 and 89).

4. Carbonate Ions, $\text{CO}_3^{=}$ (see Note 90). a. In a microbeaker place 2 drops of the prepared solution, acidify with dilute H_2SO_4 and *at once* hold a drop of $\text{Ba}(\text{OH})_2$ solution (in the tip of a glass tube) inside the beaker. Warm the solution on the steam bath, and observe the drop of $\text{Ba}(\text{OH})_2$ solution.

White Precipitate or Cloudiness

in the $\text{Ba}(\text{OH})_2$ solution indicates $\text{CO}_3^{=}$ present (see Note 91).

5. Cyanide Ions, CN^- . a. Place 2 drops of the prepared solution in a microbeaker and acidify with dilute H_2SO_4 . Hold a very small drop of $(\text{NH}_4)_2\text{S}_x$ solution in the end of a glass tube and lower it inside the beaker to within a short distance of the solution. Warm the solution gently for 30 to 60 sec. (*do not boil*). Withdraw the tube, then holding the drop high above a small flame, evaporate it barely to dryness. Dip the end of the tube in 1N HCl and stir to dissolve the residue off the tube. To the solution so obtained add 1 drop FeCl_3 solution.

Red Coloration

indicates that CN^- are present.

b. If $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ are absent, the following test may be worked successfully:

To 1 drop of the solution add 1 drop FeCl_3 solution, make alkaline with NaOH , and heat for 3 to 5 min. Acidify with dilute HCl .

Dark Blue Color or Precipitate

indicates that CN^- ions are present (see Note 92).

GROUP II ANIONS

This group may contain SCN^- , $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, Cl^- , Br^- , and I^- . Using the solution prepared for this group, test 1 drop with 1 drop AgNO_3 and 1 drop conc. HNO_3 . A white precipitate indicates Group II present. In such case, perform the following tests (see Note 93).

1. **Thiocyanate Ions, SCN^- .** a. To 1 drop of the prepared solution add 1 drop FeCl_3 solution.

Red Coloration

indicates that SCN^- ions are present (see Note 94).

b. To 1 drop of the prepared solution, add 1 drop Co^{++} test solution and 3 drops amyl alcohol. Shake vigorously, then examine the alcohol layer.

Blue Layer

indicates SCN^- ions are present.

c. To 3 drops of the prepared solution, add a *mixture* of 1 drop Zn^{++} test solution, 1 drop HgCl_2 solution, and 1 drop of Co^{++} test solution. Rub the inside of the container with the tip of a stirring rod and set aside.

Blue Precipitate

indicates SCN^- are present (see Note 95).

2. **Ferricyanide Ions, $\text{Fe}(\text{CN})_6^{3-}$.** a. To 1 drop of the prepared solution add 1 drop ferrous ammonium sulfate solution.

Blue Color or Precipitate

indicates probable presence of $\text{Fe}(\text{CN})_6^=$ ions. A pale blue precipitate slowly turning darker on exposure to air indicates $\text{Fe}(\text{CN})_6^=$ instead of $\text{Fe}(\text{CN})_6^=$.

b. To 1 drop of the prepared solution add 1 drop AgNO_3 solution.

Orange Precipitate

indicates that $\text{Fe}(\text{CN})_6^=$ are present.

To the precipitate add 2 to 3 drops 6N NH_4OH . If the precipitate dissolves readily, it may be considered confirmation for the above, in the absence of $\text{CrO}_4^=$ and $\text{AsO}_4^=$.

3. Ferrocyanide Ions, $\text{Fe}(\text{CN})_6^=$. a. To 1 drop of the prepared solution add 1 drop FeCl_3 solution.

Deep Blue Color or Precipitate

indicates that $\text{Fe}(\text{CN})_6^=$ are present.

4. Iodide Ions, I^- . a. To 2 drops of the prepared solution add 1 drop bromine water. Add 4 to 5 drops of CCl_4 and shake vigorously.

Violet or Pink

layer of CCl_4 indicates I^- are present.

5. Bromide Ions, Br^- (see Note 96). a. To 2 drops of the prepared solution add 2 drops H_2O_2 and 5 drops CCl_4 , and shake the mixture vigorously.

Yellow or Brown Layer

of CCl_4 indicates that Br^- ions are present.

6. Chloride Ions, Cl^- . a. To 1 drop of the prepared solution add 2 drops AgNO_3 solution. Filter, discarding the filtrate, and wash the precipitate.

To the precipitate add 2 drops 1N NH_4OH . Stir once and filter *at once*. To 1 drop of filtrate on a watch glass with a black background add 1 drop 6N HNO_3 .

White Precipitate

indicates that Cl^- are present (see Note 97).

GROUP III ANIONS

This group consists of $\text{CrO}_4^{=}$, $\text{Cr}_2\text{O}_7^{=}$, $\text{SO}_4^{=}$, $\text{SiO}_3^{=}$, F^- , $\text{AsO}_3^{=}$, $\text{AsO}_4^{=}$, $\text{PO}_4^{=}$ and $\text{B}_4\text{O}_7^{=}$. To test for presence of the group, add 2 drops 1N NH_4Cl to 2 drops of the prepared solution and filter. To the filtrate add 2 drops 6N NH_4OH and 1 drop $\text{BaCl}_2 \cdot \text{CaCl}_2$ reagent. A precipitate indicates that Group III is present. In such case, using separate portions of the solution prepared for this group, perform the following tests:

1. Chromate, $\text{CrO}_4^{=}$, and Dichromate, $\text{Cr}_2\text{O}_7^{=}$, Ions (see Note 98). *a. Extinguish any flames nearby.* To 2 drops of the prepared solution in a microbeaker add ether to form a layer about 4 mm. deep. Then add 1 drop saturated ammonium acetate solution, 1 drop 6N H_2SO_4 , and 1 drop H_2O_2 . Place the thumb over the top of the microbeaker and shake. Observe the ether and the aqueous solution.

Blue Ether Layer and/or Green Water Solution

indicates $\text{CrO}_4^{=}$ are present.

b. In the absence of $\text{AsO}_4^{=}$, perform the following test: To one drop of the prepared solution on a spot plate, add 1 drop 6N acetic acid, 2 drops saturated ammonium acetate solution, and 1 drop 50 per cent AgNO_3 solution.

Red or Red-brown Precipitate

indicates $\text{CrO}_4^{=}$ are probably present (see Note 99).

2. Sulfate Ions, $\text{SO}_4^{=}$. *a.* To 2 drops of the prepared solution on a watch glass with a black background add 1 drop 6N HNO_3 and 1 drop BaCl_2 solution. Rub the glass lightly with the tip of a stirring rod and let stand.

White Precipitate

indicates that $\text{SO}_4^{=}$ are present.

b. To confirm a test obtained in (a), filter off the white precipitate, discarding the filtrate. Mix the precipitate with twice its volume of Na_2CO_3 , add enough water to make a paste, and transfer to a charcoal block. Heat strongly with the *reducing* flame of a blowpipe for 1 to 2 minutes. Transfer the mixture to a freshly polished silver coin, moisten with 1 to 2 drops of distilled water, and let stand for 15 min. Wash the coin with distilled water.

Yellowish or Brown Spot

on the coin proves that $\text{SO}_4^{=}$ are present (see Note 100).

3. Silicate Ions, $\text{SiO}_3^{=}$. a. Evaporate 5 drops of the prepared solution to dryness. Scrape the residue loose with the tip of a stirring rod, transfer to a small lead dish, and mix with an equal volume of pure CaF_2 or Na_2F_2 . Place on the steam bath, add 1 drop concentrated H_2SO_4 , and hold a drop of water in a tiny loop of platinum wire close to the mixture. Warm the mixture for 2 to 3 min. and observe the drop of water.

Turbidity

in the drop of water indicates that $\text{SiO}_3^{=}$ are present.

4. Fluoride Ions, F^- . a. Place 5 drops of the prepared solution in a microbeaker, make it slightly alkaline with dilute NaOH , and evaporate to dryness. Cool, then add 2 drops concentrated H_2SO_4 to the residue. Warm gently, holding a small drop of water in the tip of a glass tube inside the beaker a few millimeters above the mixture. Observe the drop of water.

Turbidity

in the water indicates F^- are present.

b. Confirm any test obtained in (a) by washing and drying both the glass tube and the microbeaker and examining the surfaces of both.

Frosted or Etched

appearance inside the beaker or on the end of the glass tube confirms the presence of F^- .

5. Arsenite, $AsO_3^{=}$ and Arsenate, $AsO_4^{=}$, Ions. *a.* In the absence of other metals of Group II, perform the following test:

To 3 drops of the prepared solution add dilute HCl until all the Ag^+ added in the preliminary treatment are precipitated as AgCl. Filter, discarding the precipitate, and evaporate the filtrate barely to dryness. Dissolve the residue in 0.3*N* HCl and pass in H_2S for 30 sec.

Yellow Precipitate

forming *immediately* indicates that $AsO_3^{=}$ are present.

— — — — —

If no immediate precipitation takes place, add 2 to 3 crystals of NH_4I , heat almost to boiling, and saturate with H_2S .

Yellow Precipitate

indicates the presence of $AsO_4^{=}$ (see Note 101).

b. To 2 drops of the prepared solution, add NH_4Cl solution until all the Ag^+ are precipitated as AgCl. Filter, discarding precipitate. To the filtrate, add 1 drop Cu^{++} test solution and an excess of 6*N* NaOH, and boil.

Blue Solution forming a Yellow or Red Precipitate of Cu_2O , on boiling, indicates that $AsO_3^{=}$ are present (see Note 102).

— — — — —

A bluish-green precipitate obtained by the above treatment, insoluble in excess NaOH and giving no yellow or red precipitate, indicates the probable presence of $AsO_4^{=}$ and the absence of $AsO_3^{=}$.

c. In the absence of $CrO_4^{=}$ or $PO_4^{=}$, use the following tests:

To 1 drop of the prepared solution add 1 drop AgNO_3 and 2 drops saturated ammonium acetate.

Curdy Yellow Precipitate

indicates that $\text{AsO}_3^=$ are present, and $\text{AsO}_4^=$ are absent.

Chocolate-colored Precipitate

indicates that $\text{AsO}_4^=$ is present. $\text{AsO}_3^=$ may be present or absent.

6. Phosphate Ions, $\text{PO}_4^=$. If arsenites and arsenates are present, they should be removed before performing the following tests. The procedure is the same as that used in precipitating the sulfides of the Group II metals (which see). The filtrate from the H_2S precipitation (or the prepared solution, if $\text{AsO}_3^=$ and $\text{AsO}_4^=$ are absent) is used as follows:

a. Make 2 drops of the solution slightly basic with 6*N* NH_4OH (see Note 103). Add 1 drop magnesia mixture, rub the inside of the container with a stirring rod, and set aside for about 15 min.

White Crystalline Precipitate

indicates that $\text{PO}_4^=$ are present.

b. To 2 drops of the solution add NH_4Cl and filter to remove Ag^+ . To the filtrate add 1 drop 6*N* HNO_3 and 1 drop ammonium molybdate reagent. Warm on the steam bath 2 to 3 min. and set aside for about 15 min.

Yellow Precipitate

indicates $\text{PO}_4^=$ are present.

c. In the absence of $\text{CrO}_4^=$ (and $\text{AsO}_3^=$ and $\text{AsO}_4^=$), use the following test:

To 1 drop of the solution add 1 drop AgNO_3 solution and 2 drops saturated ammonium acetate solution.

Yellow Precipitate

indicates $\text{PO}_4^=$ are present.

7. Borate, BO_3^- , and Tetraborate, B_4O_7^- , Ions (see Note 104). *a.* Place 3 drops of the prepared solution on a Pyrex watch glass or a crucible lid, add 1 drop 6*N* NaOH, and evaporate just to dryness. Cool, add 1 drop of concentrated H_2SO_4 and 3 to 4 drops methyl alcohol. Stir, then ignite the alcohol.

Yellow-green Tinge

to the flame indicates these ions are present (see Note 105).

b. To 1 drop turmeric solution on a crucible lid add 1 drop 1*N* HCl and 1 drop of the prepared solution. Evaporate to dryness, *very cautiously*.

Red-brown Spot

indicates the presence of these ions.

GROUP IV ANIONS

This group consists of NO_3^- , $\text{C}_2\text{H}_3\text{O}_2^-$, ClO_3^- , and MnO_4^- ions. The tests for the members of this group should be made on the special solutions prepared for the ions to be identified.

1. Nitrate Ions, NO_3^- . *a.* To 5 to 10 drops of the prepared solution in a microbeaker add 5 drops ferrous ammonium sulfate and stir. Tilt the tube at a 45-degree angle and by means of a medicine dropper let 5 to 6 drops of concentrated H_2SO_4 run down the side of the beaker to form a layer under the solution.

Reddish or Brown Ring

at the interface between the two liquids indicates that NO_3^- are present (see Note 106).

b. In the absence of ferric, chlorate, and other oxidizing ions the following test (due to Lunge) may be used (65):

Place 1 drop of the prepared solution on a glass slide or spot plate. Beside it, place 1 drop of diphenylamine reagent, and, with a stirring rod, draw the solution into contact with the reagent.

Blue Color

at the interface between the liquids indicates that NO_3^- are present.

2. Acetate Ions, $\text{C}_2\text{H}_3\text{O}_2^-$. *a.* To 2 drops of the prepared solution in a 4-in. test tube add 1 drop ethyl alcohol and 1 drop dilute H_2SO_4 . Plug the top of the test tube with cotton, place the test tube on the steam bath, and warm 4 to 5 min. Remove the cotton plug and smell the vapors coming from the mixture.

Fruity Odor

indicates $\text{C}_2\text{H}_3\text{O}_2^-$ are present. (*Caution:* It is best to run a blank reaction at the same time. Otherwise, the odor of the alcohol may be misleading.)

b. To 1 drop of the prepared solution on a spot plate add 1 drop saturated iodine solution and 1 drop 5 per cent lanthanum nitrate solution. Let stand for 1 to 2 min., then add 1 drop 1N NH_4OH .

Bluish Coloration

indicates $\text{C}_2\text{H}_3\text{O}_2^-$ (see Note 107).

3. Chlorate Ions, ClO_3^- . *a.* Place 3 drops of the prepared solution in a microbeaker, make it strongly alkaline with NaOH solution, and add 3 to 4 granules of aluminum to the solution. Place the beaker on the steam bath and heat for 5 to 10 min. Cool, acidify with dilute HNO_3 , and add 1 drop AgNO_3 solution.

White Precipitate

indicates that ClO_3^- is present (see Note 108).

4. Permanganate Ions (MnO_4^-). *a.* If manganese was found during the cation analysis of this unknown, a violet color in the solution indicates that MnO_4^- are present. A colorless solution indicates that MnO_4^- are absent.

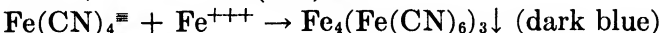
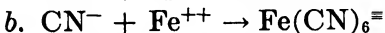
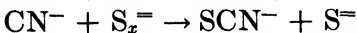
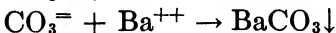
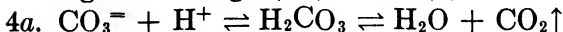
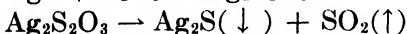
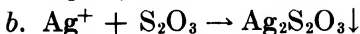
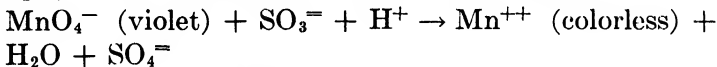
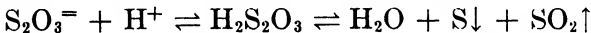
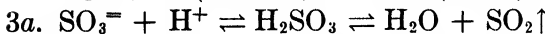
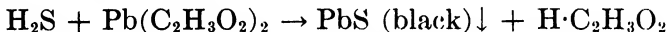
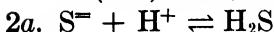
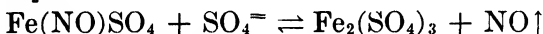
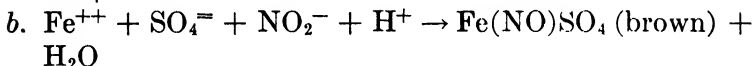
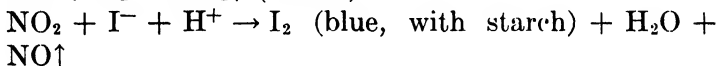
b. To 3 drops of the prepared solution (if it is violet in color) add 1 drop dilute H_2SO_4 . Then add, drop by drop, some 3 per cent H_2O_2 .

Fading of Violet Color

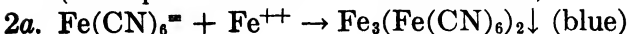
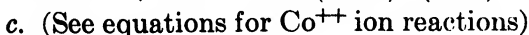
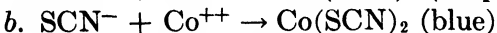
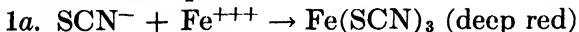
with evolution of oxygen, confirms the presence of MnO_4^- (Note 109).

EQUATIONS FOR REACTIONS OF ANIONS

Anion Group I:



Anion Group II:



- b. $\text{Fe}(\text{CN})_6^{=} + \text{Ag}^+ \rightarrow \text{Ag}_3\text{Fe}(\text{CN})_6\downarrow$ (orange)
- 3a. $\text{Fe}(\text{CN})_6^{=} + \text{Fe}^{+++} \rightarrow \text{Fe}_4(\text{Fe}(\text{CN})_6)_4\downarrow$ (dark blue)
- 4a. $\text{I}^- + \text{Br}_2 \rightarrow \text{I}_2 + \text{Br}^-$
- b. $\text{Cu}^{++} + \text{I}^- \rightarrow \text{CuI}_2$
 $\text{CuI}_2 \rightarrow \text{Cu}_2\text{I}_2\downarrow$ (white) + I_2 (violet in CCl_4)
5. $\text{Br}^- + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Br}_2$ (yellow in CCl_4) + H_2O
- 6a. $\text{Cl}^- + \text{Ag}^+ \rightarrow \text{AgCl}\downarrow$ (white, soluble in NH_4OH)
 $\text{Br}^- + \text{Ag}^+ \rightarrow \text{AgBr}\downarrow$ (yellowish, insoluble in NH_4OH)
 $\text{I}^- + \text{Ag}^+ \rightarrow \text{AgI}\downarrow$ (yellowish, insoluble in NH_4OH)

Anion Group III:

- 1b. $\text{CrO}_4^{=} + \text{Ag}^+ \rightarrow \text{Ag}_2\text{CrO}_4\downarrow$ (red-brown)
- 2a. $\text{SO}_4^{=} + \text{Ba}^{++} \rightarrow \text{BaSO}_4\downarrow$ (white)
- b. $\text{BaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{BaCO}_3\downarrow + \text{Na}_2\text{SO}_4$
 $\text{Na}_2\text{SO}_4 + \text{C} \rightarrow \text{Na}_2\text{S} + \text{CO}\uparrow$
 $\text{Na}_2\text{S} + \text{Ag} + \text{H}^+ + \text{O}_2 \rightarrow \text{Na}^+ + \text{H}_2\text{O} + \text{Ag}_2\text{S}\downarrow$ (brown or black)
3. $\text{Na}_2\text{F}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{F}_2 + \text{Na}_2\text{SO}_4$
 $\text{H}_2\text{F}_2 + \text{SiO}_3^{=} \rightarrow \text{SiF}_4\uparrow + \text{H}_2\text{O} + \text{F}^-$
 $\text{SiF}_4 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SiF}_6 + \text{H}_4\text{SiO}_4\downarrow$ (white)
4. [Same as (3).]
- 5a. $\text{AsO}_3^{=} + \text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3\downarrow$ (yellow) + H_2O
 $\text{AsO}_4^{=} + \text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_5\downarrow$ (yellow) + H_2O
 $\text{AsO}_4^{=} + \text{I}^- + \text{H}^+ \rightarrow \text{As}^{+++} + \text{H}_2\text{O} + \text{I}_2$
- b. $\text{Cu}(\text{OH})_2 + \text{AsO}_3^{=} \rightarrow \text{Cu}_2\text{O}\downarrow$ (red) + $\text{AsO}_4^{=} + \text{H}_2\text{O}$
 $\text{Cu}(\text{OH})_2 + \text{AsO}_4^{=} \rightarrow \text{Cu}_3(\text{AsO}_4)_2\downarrow$ (bluish green) + OH^-
- c. $\text{AsO}_3^{=} + \text{Ag}^+ \rightarrow \text{Ag}_3\text{AsO}_3\downarrow$ (yellow)
 $\text{AsO}_4^{=} + \text{Ag}^+ \rightarrow \text{Ag}_3\text{AsO}_4\downarrow$ (chocolate brown)
- 6a. $\text{PO}_4^{=} + \text{Mg}^{++} + \text{NH}_4^+ \rightarrow \text{MgNH}_4\text{PO}_4\downarrow$ (white)
- b. $\text{PO}_4^{=} + \text{NH}_4^+ + \text{MoO}_4^{=} + \text{H}^+ \rightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3\downarrow$ (yellow) + H_2O

PROBLEMS

1. What weight of each of the following substances would be required to prepare 100 ml. of a 0.4*M* solution of each? What weight would be required to prepare 100 ml. 0.4*N* solution?

(a) NaCl

(d) $\text{Fe}_2(\text{SO}_4)_3$

(b) KOH

(e) HNO_3

(c) H_3PO_4

(f) $\text{HC}_2\text{H}_3\text{O}_2$

2. If 25 ml. of 0.2*N* NaOH solution is required to neutralize 40 ml. of a solution of H_2SO_4 , what is the normality of the acid? What is its molarity?

3. A solution is prepared by diluting 25 ml. of an acid to a volume of 100 ml. Thirty milliliters of this diluted acid will neutralize 75 ml. of 0.8*N* KOH solution. What is the normality of the original acid?

4. A solution is prepared by adding 10 ml. concentrated H_2SO_4 to 50 ml. water and diluting the resulting solution to a total volume of 180 ml. On trial, it is found that 50 ml. of this solution will neutralize 200 ml. of 0.5*N* NaOH solution. (a). What was the normality of the concentrated H_2SO_4 ? (b). What was its molar concentration? (c). What weight of H_2SO_4 is there in 1 liter of the concentrated H_2SO_4 ?

5. A certain solution of H_2SO_4 has a specific gravity of 1.5263 and is 62.18 per cent H_2SO_4 by weight. What is the (a) molar and (b) normal concentration of this acid?

6. A solution of CuSO_4 , having a specific gravity of 1.206 is 20 per cent CuSO_4 by weight. What is its (a) molar and (b) normal concentration?

7. What is the maximum equilibrium concentration of Ag^+ ions that can exist in a solution containing 0.01 mol per liter of I^- ions?

8. What is the maximum concentration of CO_3^{2-} that can be added to 0.1*M* AgNO_3 solution without causing Ag_2CO_3 to precipitate?

9. Silver nitrate solution is added slowly, drop by drop, to a solution which is 0.1*M* with K_2CrO_4 and 0.01*M* with NaCl. What will be the concentration of the first ion, at the moment the second ion first begins to precipitate?

10. A solution is 0.1*M* with $\text{Pb}(\text{NO}_3)_2$, 0.01*M* with AgNO_3 , 0.1*M* with $\text{Hg}(\text{NO}_3)_2$, 0.1*M* with $\text{Fe}(\text{NO}_3)_2$, and 0.1*M* with $\text{Mn}(\text{NO}_3)_2$. If H_2S is passed into the solution until precipitation is complete and until the sulfide ion concentration in the solution at the end is 10^{-22} mol per liter, which of the metallic sulfides will have precipitated? What will be the concentration of each metallic ion in the final solution?

11. From calculations using the solubility product constants of AgI, AgBr, Ag_2CO_3 , Ag_2CrO_4 , and AgCN, list these compounds in the order of

decreasing concentrations of Ag^+ needed to precipitate these compounds from 0.1M solutions of I^- , Br^- , CO_3^{2-} , CrO_4^{2-} , and CN^- .

12. The solubility of CaCrO_4 is 14.1 g. per liter. Calculate its solubility product constant.

13. The solubility of SrC_2O_4 is 0.05 g. per liter. Calculate its solubility product constant.

14. From the solubility product constants of the following substances, calculate their solubilities in (a) mols per liter; (b) grams per liter; (c) grams per 100 cc.

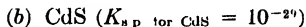


15. The solubility of $\text{Ca}_3(\text{PO}_4)_2$ is 0.02 g. per liter. What is its solubility product constant?

16. The solubility of CaHPO_4 is 0.2 g. per liter. What is its solubility product constant?

17. From the solubility product constants of CdS and ZnS calculate the efficiency with which Cd^{++} and Zn^{++} may be separated using H_2S as the reagent.

18. In the 0.3N HCl solution used during the precipitation of the Group II metals it is possible for the H_2S to furnish S^{2-} in concentrations as high as 10^{-21} molar. The usual unknown in Group II contains each ion at a concentration of 0.02 mol per liter. With these points in mind, what would be the concentration of the following ions left in the filtrate at the end of the Group II precipitation?



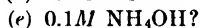
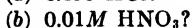
19. Show by calculations that it is possible to precipitate ZnS in the second group if the concentration of Zn^{++} in the solution is greater than 1.2×10^{-2} mol per liter.

20. What is the hydrogen ion concentration in a 0.1M solution of HCN ? Of 0.01M HCN ?

21. What is the hydrogen ion concentration in a 0.1M solution of $\text{H}\cdot\text{C}_2\text{H}_3\text{O}_2$? Of 0.01M $\text{H}\cdot\text{C}_2\text{H}_3\text{O}_2$? Of 0.000001M $\text{H}\cdot\text{C}_2\text{H}_3\text{O}_2$? (HINT: Remember Arrhenius' theory.)

22. What is the hydroxyl ion concentration in 0.1M NH_4OH ? In 0.001M NH_4OH ?

23. What is the hydrogen ion concentration in each of the following solutions:



24. What is the hydrogen ion concentration in a solution that is 0.1M with $\text{NaC}_2\text{H}_3\text{O}_2$ and 0.01M with $\text{H}\cdot\text{C}_2\text{H}_3\text{O}_2$? One that is 0.1M with $\text{NaC}_2\text{H}_3\text{O}_2$ and 0.1M with $\text{HC}_2\text{H}_3\text{O}_2$?

25. What is the hydroxyl ion concentration in each of the following solutions:

- (a) A solution $0.1M$ with NH_4Cl and $0.01M$ with NH_4OH ?
 (b) A solution $0.1M$ with NH_4Cl and $0.1M$ with NH_4OH ?

26. What would be the hydroxyl ion concentration in a solution made by mixing equal volumes of the solution in Problem 25 (a) and distilled water? Work the same problem for Problem 25 (b).

27. At the beginning of the Group III precipitation, the unknown is made strongly basic with NH_4OH and then NH_4Cl is added. Assuming that the resulting solution is $2M$ with NH_4Cl and $1M$ with NH_4OH what is the *hydrogen ion concentration* of the solution? If the $K_{a.p. H_2S} = 10^{-23}$, what is the maximum S^{2-} concentration, in this solution, obtainable by adding H_2S to the solution?

28. Using the answer obtained in Problem 27, calculate the concentration of Fe^{++} ion, of Mn^{++} and of Zn^{++} left in the filtrate after the Group III precipitation has been completed.

29. Show by calculation that H_2S will precipitate Cu^{++} from a solution $0.1M$ with $Cu(NO_3)_2$ and $1M$ with HCl .

30. What is the hydrogen ion concentration in a $0.2M$ solution of NH_4Ac to which has been added an equal volume of

- (a) $0.02M$ HCl ? (c) $0.02M$ $NaOH$?
 (b) $0.18M$ HCl ? (d) $0.18M$ $NaOH$?

From these results could you call NH_4Ac a universal buffering agent?

31. A solution is made by mixing equal volumes of $0.22M$ acetic acid and $0.20M$ NH_4OH . What is the hydrogen ion concentration of the resulting solution? What is its hydroxyl ion concentration?

32. What is the pH of each of the following solutions:

- (a) $0.1M$ HCl ? (c) $0.003M$ NH_4OH ?
 (b) $0.5M$ $NaOH$? (d) A solution that is made $0.1M$ with NH_4Cl and $0.01M$ with KOH ?

33. What is the electrode potential of a combination of a normal manganese half-cell and a normal antimony half-cell?

34. If a cell is made up of two half-cells which contain the same elements, the concentration of the ions in the two being different, the electromotive force of the combination is given by the expression

$$E.m.f. = \frac{0.059}{n} \log \frac{C_1}{C_2}$$

where n is the valence of the ion involved, and C_1 and C_2 are the molar concentrations of the ions in the respective half-cells.

Using this expression calculate the electromotive force of the following combinations:

(a) $0.1M$ Cu^{++} against $0.00001M$ Cu^{++} .

(b) $0.1M$ Ag^+ against $0.00001M$ Ag^+ .

(c) $0.001M$ Cu^{++} against $0.001M$ Cu^{++} .

35. Using the simplified expression by Bronsted and La Mer, calculate the ionic strength μ of

(a) $0.01M$ $NaCl$.

(b) $0.001M$ $CuCl_2$.

NOTES ON ANALYTICAL PROCEDURE

1. If the unknown is an alloy the water treatment may be omitted here. However, if it is necessary to carry the alloy through a fusion, the fused substance should be tested with water as instructed.

2. Nitric acid is used before hydrochloric acid, owing to the fact that, if any of the metals of Group I are present, they will cover the sample with an insoluble coating of the metallic chloride and render its solution difficult.

3. Aqua regia is sometimes prepared by mixing one volume of concentrated nitric acid with three volumes of *concentrated* HCl. It must *always* be prepared just before using as it decomposes very quickly on standing.

4. If the unknown is an alloy containing tin, a white residue of meta-stannic acid is often left at this point. This should be treated with hot concentrated HCl for a few minutes, then filtered and the residue treated with water, the filtrates being combined with the other filtrates (see Amphoteric Hydroxides).

A mineral should receive the above treatment at this point, in any case, as any white residue may appear colored owing to the presence of dark-colored substances in the mixture.

5. If the analysis is to be made for silicon and sodium, it is necessary to use a crucible made of some other material, as part of the crucible itself reacts with the fusion mixture, and the crucible contains these materials. Iron or, even better, nickel crucibles can be used in such cases. If a complete analysis is desired it is best to conduct two fusions, using one kind of crucible for the first and another for the second. Those elements, found in *both cases*, may be assumed to be present in the unknown sample.

6. The filtrate from the aqueous extraction of the fusion mixture should be acidified with dilute HNO_3 , heated 2 to 3 min. and filtered. The filtrate should be combined with the other filtrates as before. The precipitate is silicic acid, its source being either the unknown, or, if a porcelain crucible was used for the fusion, the glazed surface of the crucible. In the latter case, the precipitate should be discarded.

7. When the filtrates are combined, a white precipitate often forms especially when silver, lead, bismuth, mercury, or antimony is present. This precipitate may be due to either of two things: (a) If bismuth or antimony are present, their salts may have undergone hydrolysis to form *insoluble* basic salts of the type $\text{Bi}(\text{OH})_2(\text{NO}_3)$; (b) if the other three metals are present, their chlorides will precipitate when the chlorides from the aqua regia or hydrochloric acid treatments are mixed with the nitric acid solution containing these metallic ions.

It is necessary, in such cases, to make the solution strongly acid with concentrated hydrochloric acid. This will dissolve the hydrolytic products

of bismuth and antimony and part or all of the lead chloride (owing to the formation of complex ions of the type PbCl_2^- and PbCl_4^{2-}). The precipitate left should be used as the precipitate for the Group I analysis. Any lead or mercury that redissolves will be found in Group II.

8. When nitric and hydrochloric acids are mixed, as in aqua regia, some reaction occurs forming a mixture of chlorine, and nitrosyl chloride (NOCl), which is unstable. In dissolving substances such as HgS , therefore, two reactions are responsible for the great ability of aqua regia to put insoluble substances into solution: (a) The nitrate ions present, as well as the nitrosyl chloride, act as a powerful oxidizing agent, oxidizing sulfide ion to free sulfur and to sulfate ion; (b) chloride ions may combine with many metallic ions to form complex ions of the type HgCl_4^{2-} .

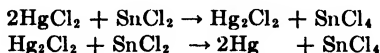
9. After precipitation seems complete scratch the inside of the beaker with a stirring rod and let stand 3 to 5 min. PbCl_2 is very slow to precipitate and may be overlooked in the group if not given plenty of time.

10. The absence of a precipitate at this point means that the metals of Group I, with the possible exception of lead, which can be found in Group II, are absent.

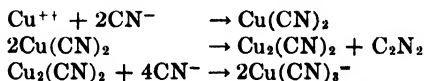
11. Lead chloride is quite soluble in hot water but reprecipitates at once if the solution is allowed to cool. The small volume of liquid used here cools very rapidly, and the test for lead is often lost through failure to keep the solution hot during the whole procedure. It is best to preheat the medicine dropper, before using it for the filtration or for transferring the solution, by placing its tip in a microbeaker full of hot water on the steam bath for a few seconds. Also the filtrate should be kept hot on the steam bath during the running of the tests for lead.

12. The gallic acid test works only with absolutely fresh gallic acid solution, 5 minutes standing being sufficient to ruin the reagent. Acid solutions render the test less sensitive, while alkaline solutions oxidize in air immediately, to give a color similar to that produced by mercury. It is necessary, therefore, to have the solution *faintly acid*—a condition best reached by buffering an acid solution with sodium acetate.

13. Stannous chloride, SnCl_2 , is a strong reducing agent. It reduces the mercuric chloride (from the aqua regia treatment) in two steps, forming mercurous chloride, a white insoluble substance, and hydrated stannic chloride. More stannous chloride reduces the mercurous chloride to black metallic mercury:



14. When cyanide ion is added to a solution containing cupric ion, two successive reactions occur. First, the ions combine to form cupric cyanide which is unstable and immediately decomposes to form insoluble cuprous cyanide and cyanogen, a *very poisonous* gas. The cuprous cyanide then reacts with more cyanide ions to form the highly soluble, extremely stable cuprocyanide ion. The reactions are



As cuprocyanide ions are very stable, their solutions contain few copper ions. Consequently, hydrogen sulfide will not precipitate the sulfides of copper from solutions of cuprocyanide ions in the presence of excess cyanide ions.

15. Sodium stannite is another example of a strong reducing agent. In this case it reduces the bismuth hydroxide to metallic bismuth (black). The solution is made by adding 6*N* NaOH, drop by drop, to 2 drops stannous chloride solution (stirring during the addition) until the precipitate of stannous hydroxide that forms just redissolves. The reactions involved in this preparation are similar to those given by zinc ions under similar conditions, stannous ions, also, being amphoteric.

When used as a reducing agent, stannite ions, SnO_2^- , are oxidized to stannate ions, SnO_3^- .

16. In the analysis of Group II, bismuth hydroxide is precipitated in this same manner in the presence of the blue copper ammonia complex. The deep color of the latter and the transparent nature of the former make it difficult to see the bismuth hydroxide in the mixture. Consequently, the student will be saved much trouble if he notes the appearance of this mixture very carefully and keeps it in mind when testing for bismuth.

17. If the reagent is allowed to remain in this alkaline solution, it will slowly deposit a yellow precipitate even in the absence of Cd^{++} ions. This takes a few minutes, however, and as the coloration appears quickly in the presence of cadmium, this phenomenon need not cause trouble. In case of doubt, however, it is best to run a blank test for comparison.

18. The precipitation of As_2S_5 from solutions of arsenic ions, As^{++++} , by means of hydrogen sulfide, is very slow except in hot, strongly acid solutions. High acidity is prohibited in this separation, as the sulfides of some of the other Group II metals would not precipitate in highly acid solutions. Therefore, use is made of the fact that arsenious sulfide is easily precipitated from solutions of arsenious ion, arsenic ions being reduced by NH_4I to the arsenious state and then the H_2S being added.

The reduction is preceded by a preliminary precipitation with hydrogen sulfide, however, as it is essential that the tin present be precipitated before reduction. As stannous sulfide is not soluble in ammonium monosulfide $(\text{NH}_4)_2\text{S}$, any tin that is present as stannous ions will be overlooked.

19. Insoluble As_2S_3 and SnS_2 react with the sulfide ions from ammonium monosulfide to form the complex ions AsS_3^- , SbS_3^- and SnS_3^- . These ions decompose if *weakly* acidified, to form the original sulfides and hydrogen sulfide.

Ammonium monosulfide, $(\text{NH}_4)_2\text{S}$, should be prepared *fresh* each laboratory period, as it quickly oxidizes to ammonium polysulfide, $(\text{NH}_4)_2\text{S}_x$, a reagent which dissolves not only the above sulfides but also, to some extent, the sulfides of mercury, copper and bismuth. The reagent is prepared by

passing a rapid stream of hydrogen sulfide through 3 ml. 6*N* NH_4OH for about 3 min.

20. The product of the evaporation of As_2S_3 with aqua regia will be arsenic oxide which is produced by the hydrolysis of the AsCl_3 first formed and the loss of hydrogen chloride during evaporation. As As_2O_3 is somewhat volatile, prolonged or intensive heating at this point should be avoided.

21. The experiment described here is a modification of the Gutzeit test for arsenic. It depends upon the reduction of the arsenic, by means of the sodium hydroxide and aluminum, to arsine, AsH_3 , a gas which reacts with the silver nitrate giving a brownish stain of silver, arsenic, and complexes of these elements. The test works best if, before the sodium hydroxide is added, the residue of arsenic pentoxide is reduced to the arsenious state by the addition of HCl and sodium bisulfite, NaHSO_3 , solution.

22. This is another example of a hydrolysis reaction (see page 26 and Note 7). It is reversed if a strong acid is added to the mixture.

23. The change of color of the cacotheline is due to its reduction by the stannous ion to a new dye. The success of this test depends upon the successful reduction of the stannic ion to the stannous state by the treatment with acid and aluminum or with zinc.

24. An unusually successful way to carry out the reduction of the Sn^{++++} ions is as follows:

In a 4 by $\frac{1}{2}$ -in. test tube put the solution to be tested. Make it strongly acid with HCl and add 2 to 3 granules of zinc or aluminum. In the top of the tube, suspend a 3 by $\frac{3}{8}$ -in. test tube, two-thirds full of cold water; then heat the solution in the larger test tube *very gently*, keeping it as hot as is possible without causing the mixture to boil over. When the metal is all dissolved, use the solution for the usual tests.

The advantage of this method is that it prevents, by condensation, the escape of HCl and water, and it prevents the entrance of air into the reaction mixture. The reduction proves to be more dependable using this method.

25. It is essential that the residue from this evaporation be not overheated. Certain metallic salts, such as those of iron, hydrolyze readily and, in evaporations such as this, are converted to the oxides. Many of these oxides are changed, by heating, into forms which are only slowly soluble in 0.3*N* HCl and thus may be found mixed with the Group II precipitate. This results in the tests for members of Group II being spoiled and in failure to find certain metals in later groups. Certain ions in the second group, such as those of bismuth, antimony and tin, remain undissolved in the 0.3*N* HCl ; but if the evaporation is carefully accomplished, this residue need not worry the student. It is only necessary to continue the treatment with hydrogen sulfide until all the original residue has changed color—becoming either black, orange, or yellow.

26. This process will give a solution whose acidity is approximately that of 0.3*N* HCl , all excess acid being lost during the evaporation.

27. The sulfides of certain metallic ions (arsenic, cobalt and nickel are notable examples) tend to *peptize* readily, i.e., go from a precipitate to a colloidal form. Others, of only moderately low solubility (such as cadmium),

partly redissolve in water. This wash solution opposes both these tendencies, the ammonium nitrate neutralizing the charges on the colloidal particles (see page 34) and the sulfide ions from the hydrogen sulfide preventing much of the metallic sulfide going into solution (see page 32). The $\text{NH}_4\text{NO}_3\text{-H}_2\text{S}$ solution should be prepared fresh by passing H_2S through 1 ml. NH_4NO_3 solution for 1 min.

28. Much information can be gleaned by observing the appearance of the mixture during various stages of the precipitation of the Group II sulfides. No precipitate, of course, means that these metals are all absent. A yellow precipitate means that lead, copper, bismuth, and mercury are absent, as their sulfides are black. A heavy yellow precipitate, forming immediately upon adding H_2S to the solution after treatment with NH_4I , indicates the probable presence of As^{++++} .

These indications cannot be taken as tests for these ions; but their appearance often serves as a warning of something having gone wrong, if the test for the element does not appear later.

29. In case a large quantity of precipitate is found in Subgroup II B, the treatment of the precipitate with ammonium monosulfide should be repeated until all members of the tin group are dissolved out.

30. In general, the solubilities of salts in alcohol or mixtures of alcohol and water are lower than in water itself. Thus, by adding alcohol, redissolving of the PbSO_4 may be prevented. Sometimes a hydrolysis product of bismuth sulfate precipitates out at this point. However, if the solution is allowed to stand only 2 min., the bismuth salt will not come down as it supersaturates readily.

31. If the precipitate is light in color or remains floating on top the liquid, it is most likely sulfur, and the tests for mercury may be omitted.

32. It is essential that a moderate *excess* of NH_4OH be added here, and that the solution be stirred thoroughly as $\text{Cu}(\text{OH})_2$ may otherwise not redissolve, and both the copper and bismuth may be overlooked.

33. Whether copper is present or not, the CdS precipitate may be colored black due to traces of lead or bismuth which have escaped removal. Consequently, the following procedure is usually more successful in detecting cadmium. Proceed as follows:

Take the remainder of the ammoniacal solution from the bismuth and copper tests and evaporate barely to dryness. Dissolve the residue in 4 drops 3N HCl and pass in H_2S until precipitation of any dark colored sulfides is complete. Centrifuge, using a cotton plug, and discard the precipitate. To the filtrate add 2 drops 6N NH_4OH and 1 drop ammonium acetate and pass in more H_2S . A **YELLOW PRECIPITATE** indicates that Cd^{++} are present. Confirm as directed in the original procedure using thiosinamine.

34. If the FeS type of generator is used, the outlet tube should be thoroughly cleaned and fresh cotton should be placed in the filter bulb of the delivery tube each laboratory period. Otherwise, spray may carry traces of iron into the unknown, and, since the tests for iron are very sensitive, it may be found, even though the unknown originally contained none. It

may be necessary to use a wash bottle with this apparatus if contamination appears.

35. If, on acidification, traces of precipitate appear at first but dissolve later, it is probable that too much acid has been added. In that case, the solution should be tested with litmus and, by addition of 1*N* NH_4OH , brought to a weakly alkaline condition. One normal HCl should again be added (with stirring) until the solution is very faintly acidic to litmus.

36. If the precipitate refuses to settle or is very pale yellow (almost white), it is probably sulfur and the members of the tin group may be considered absent.

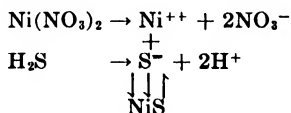
37. In carrying out this modified Gutzeit test for arsenic, it is necessary to avoid direct sunlight, H_2S in the air, or NH_3 fumes. Any of these will darken the AgNO_3 spot giving it a color similar to that obtained in the presence of arsenic.

38. A yellow precipitate forming after some time, here, may be disregarded. It is probably stannic sulfide, which will precipitate under these conditions if present in large concentration.

39. It is essential that all the aluminum be removed from the solution, either by letting the excess metal dissolve in acid or by filtration. If this is not done, the metal and acid will reduce the cacotheline and give the test for tin whether the latter is present or not.

40. In both the precipitation, and the Gutzeit test for arsenic, it is best to run a blank test at the same time as the regular test is being run. To do this, all of the reagents are added to a drop of distilled water as if the latter contained arsenic. By comparing the results, errors due to contamination from the air or reagents are easily avoided.

41. During this precipitation, it is necessary that a moderate excess of base be present. The reaction of a salt with hydrogen sulfide results in excess hydrogen ion being formed—as illustrated here:



This acid must be neutralized by the base in order to prevent reversal of the reaction. At the same time, the hydroxyl ion concentration must be kept low to prevent precipitation of the hydroxides of barium, calcium, strontium, and magnesium, with the metals of Group III. These apparently opposing conditions are brought about by the use of a strong solution of NH_4OH buffered with NH_4Cl . This gives a large reserve of base, but a low immediate hydroxyl ion concentration.

42. The ferric hydroxide precipitated by the hydrolysis of ammonium benzoate is more crystalline in nature and has less tendency to include portions of the solution containing the other ions.

43. A large excess of hydroxyl ion is necessary if the aluminate ions are to remain stable in solution. If the hydroxyl ion concentration is lowered

by adding a buffering agent, such as ammonium chloride, the sodium aluminate will decompose and aluminum hydroxide will precipitate. This precipitates the aluminum hydroxide without the necessity of first acidifying the solution, and avoids certain difficulties otherwise found in the analysis of chromium (see Note 46).

44. Both aluminon reagent and alizarin S (blue) reagent tend to precipitate on standing in the reagent bottle. It is therefore necessary that these reagents be freshly filtered by the student just before using. The best procedure is to take about eight drops of the reagent and centrifuge it, drawing off enough of the clear solution for the test, using a medicine dropper.

45. When chromic ion is treated with excess sodium hydroxide, a solution of sodium chromite (NaCrO_2) is formed. On addition of sodium peroxide, which is a strong oxidizing agent, the chromite ion is oxidized to chromate ion.

46. The addition of sodium peroxide to water always results in the formation of small amounts of hydrogen peroxide. Hence, when sodium chromite solution is treated with sodium peroxide, the result is a solution of chromate ion and hydrogen peroxide. If this is acidified, perchromic acid (a highly unstable, blue substance of uncertain formula) is formed, this rapidly decomposing to give oxygen and the original chromic ion, Cr^{+++} . For this reason, in the separation of chromate ion from the aluminum, a buffering agent is used to precipitate the latter instead of, as some procedures direct, first acidifying and then making the solution alkaline with ammonium hydroxide.

47. Barium chromate is soluble in strong acids. However, if such solution is treated with a buffering agent to reduce the hydrogen ion concentration of the solution, the barium chromate will reprecipitate.

48. Ammonium persulfate in the presence of silver ion is a very powerful oxidizing agent. When the HNO_3 solution of a compound of manganese is treated with this mixture, the manganese is oxidized to permanganic acid, HMnO_4 , and the persulfate ions, $\text{S}_2\text{O}_8^{--}$, are reduced to sulfate ions.

49. As mentioned earlier (see Note 27), the sulfides of cobalt and nickel have a strong tendency to peptize. The ammonium sulfate prevents the formation of these colloids by neutralizing any charges on the colloidal particles, as fast as they form.

50. Many metals give characteristic bead tests with borax, these tests often being used for confirmation tests. The test for cobalt is extremely sensitive and quite specific.

51. Cobalt gives a very light, brownish color with dimethylglyoxime if the metallic ions are present in high concentration. This coloration, however, is so weak that it will not interfere with the test for nickel in any ordinary analysis. The test for nickel as described here is sensitive to one part in a million. Dimethylglyoxime is a reagent for several other metallic ions but the interfering ions are removed before this point in the procedure.

52. Some helpful information can be gained by carefully watching the changes that occur in the unknown on the addition of the NH_4OH . A

gelatinous, reddish-brown precipitate, insoluble in excess NH_4OH , may indicate that iron is present. A colorless, gelatinous precipitate that fails to dissolve in excess NH_4OH indicates the probable presence of aluminum. No precipitate at all, in excess NH_4OH , means that both iron and aluminum are absent. If, on adding H_2S , a white precipitate appears with no other colored precipitate forming, zinc is probably present, and iron, nickel, and cobalt are absent.

53. After precipitation is apparently complete, test the solution with litmus. It should be strongly basic. If the solution is *weakly* basic or acidic, add 2 to 3 drops more 6*N* NH_4OH solution, stir and add more H_2S (see Note 41).

54. The ammonium nitrate-hydrogen sulfide solution is used here for the same purpose as in Group II (see Note 27). Ammonium sulfate cannot be used at this point as it would precipitate barium, strontium and, perhaps, calcium from the filtrate that still wets the precipitate.

55. The action of the ammonium acetate here is as described in Note 46.

56. If the aluminon reagent is weak, it may be necessary to add 8 to 10 drops instead of 3 to 5 drops.

57. If a precipitate is obtained that is not of the proper color, it is best to filter it, redissolve in dilute hydrochloric acid, add 8 to 10 drops of alizarin, and reprecipitate with ammonium hydroxide.

58. The high concentration of acetate ions, added during the precipitation of $\text{Al}(\text{OH})_3$, causes the formation of slightly soluble silver acetate and prevents the formation of Ag_2CrO_4 unless excess AgNO_3 is added. If the solution is yellow before the AgNO_3 is added and no Ag_2CrO_4 appears, it is best to add another drop of the reagent.

A white precipitate should be disregarded, as silver acetate will precipitate whether chromium is present or not. A basic solution should be avoided, also, as it would then precipitate dark-colored Ag_2O .

59. If the solution becomes somewhat milky in appearance, evaporate to half its volume and add more H_2S . ZnS readily forms colloidal solutions, so the usual precautions must be taken against this. Plenty of time should be taken for the precipitation.

60. Another portion of the solution, obtained by dissolving the ZnS , may be tested by adding 1 drop NH_4SCN solution and 1 drop pyridine to the solution. A white precipitate of $\text{Zn}(\text{C}_5\text{H}_5\text{N})_4(\text{SCN})_2$ confirms the presence of zinc. Other tests are given under Auxiliary Tests.

61. A dark brown precipitate that fails to dissolve readily in the HNO_3 is usually MnO_2 , and suggests the probable presence of Mn^{++} . This may be dissolved by adding 1 drop 6*N* HCl to the mixture and warming. If this procedure is followed, however, it is necessary to evaporate the resulting solution to half its volume, then add more concentrated HNO_3 before adding the crystals of KClO_4 . Otherwise, the HCl delays, and may even prevent, the precipitation of the manganese with KClO_4 .

62. The formation of a red or pink solution on the addition of the $\text{HgCl}_2 \cdot 4\text{NH}_4\text{SCN}$ reagent indicates that some iron is still present. The

red color may be removed by the addition of a solution of microcosmic salt or of a soluble fluoride (see page 99).

63. Barium chromate is the least soluble of the three chromates. Strontium chromate is about 500 times as soluble as barium chromate but is still quite insoluble, while calcium chromate is moderately soluble in water. Therefore, it is easy to precipitate the chromates of barium and strontium without that of calcium unless calcium is present in great concentration. The strontium chromate may then be dissolved out of the mixed precipitate in a buffered acid solution, leaving the barium salt behind. It is necessary however, that the proper buffer mixture be used, since more strongly acid solutions will dissolve barium chromate. The proper mixture is obtained by mixing equal volumes of 1*N* acetic acid and 2.5*N* ammonium acetate.

64. Heating during the addition of reagents will cause the formation of larger crystals and make filtration easier.

65. The platinum wire must be cleaned thoroughly each time before it is used. This is done by heating the wire red hot and at once plunging it into clean, concentrated HCl. This process is repeated until the wire no longer causes any color in the flame.

66. The chromates, sulfates, and oxalates of the metals are not sufficiently volatile to color the flame much. The chlorides, on the other hand, give excellent results. If the precipitate were dipped into HCl, however, it would dissolve off. The vapor treatment described will convert some of the salt to chloride and still avoid loss of precipitate.

67. Notice that whereas barium chromate was easily precipitated, strontium chromate does not precipitate until the acid is neutralized.

68. If not all the precipitate dissolves, filter and treat the residue with a fresh mixture of the acetic acid-ammonium acetate mixture.

69. Calcium oxalate, though very insoluble, has a strong tendency to supersaturate. Therefore, it is necessary to heat the solution, scratch the side of the beaker with a stirring rod, and let it stand.

70. The acidification with HCl followed by addition of ammonium hydroxide furnishes some ammonium chloride. However, caution should be used to add just enough reagent to complete the precipitation for, if too much is used, any magnesium present may precipitate and spoil the analysis of this group.

71. In place of acetic acid, HNO₃ may be used and the resulting solution evaporated. Heat strongly to dehydrate, and treat at least twice with anhydrous acetone. The Ca(NO₃)₂ dissolves, leaving Ba(NO₃)₂ and Sr(NO₃)₂ as residue. The ions are then identified by an adaptation of the procedure described.

72. It is well to recall the preliminary experiment on calcium, using this reagent, and to reread Notes 64 and 69. If a precipitate forms *at once*, it means either that some strontium has escaped precipitation earlier or that calcium is present in unusually high concentration—usually the former.

73. The reagent (*p*-nitrobenzeneazoresorcinol) is destroyed by either strongly acid or strongly basic solutions. If this occurs (indicated by the solution turning yellow on addition of the reagent), it is necessary to test

the solution with litmus and neutralize it until it is very faintly acidic, then add fresh reagent.

74. All the slightly soluble salts of potassium, ammonium, and sodium readily form supersaturated solutions. Consequently, when trying to precipitate these ions, use all the precautions possible against supersaturation.

75. This reagent is prepared by the student just before using. Make a saturated solution of sodium cobaltinitrite by shaking a couple small crystals of the solid with 3 drops water. Dilute with an equal volume of water and filter. Use at once, as the reagent decomposes in a comparatively short time.

76. When sodium cobaltinitrite solution is added to a solution containing a mixture of K^+ and Ag^+ , a yellow precipitate of $K_2AgCo(NO_2)_6$ is formed. This compound is much less soluble than is $K_2NaCo(NO_2)_6$ and is capable of detecting as little as 0.0009 mg. K^+ in a drop of solution.

77. In case sodium is present in moderately large concentrations it may be necessary to use a double thickness of cobalt glass to cut out the sodium light, in using the flame test for potassium.

78. The light from the lavender potassium flame will penetrate a piece of blue glass while the yellow light of the sodium flame will not. This makes it possible to see the potassium flame even if sodium is present. Occasionally, however, a double thickness of glass is required.

79. On heating, the cobaltinitrite ions decompose. If ammonium ions are present, the two ions react in the hot solution and the ammonium ion is destroyed. Any potassium can then be reprecipitated by adding more sodium cobaltinitrite to the cold solution. This is an excellent confirmatory test for potassium.

80. It is never to be considered an acceptable flame test if the yellow color lasts less than 30 sec., as sodium contaminations are almost invariably present, either from the glass or from the air or fingers. The platinum wire must be carefully cleaned before each test by repeated heating to redness and plunging into some clean concentrated hydrochloric acid.

81. Overheating will cause loss of the ammonium salts present as most ammonium salts decompose or volatilize on heating.

82. If the paper does not become uniformly blue, it indicates that any blue spots present are due to spattering of the sodium hydroxide. The test must then be tried with a fresh sample of unknown.

83. If the unknown is a general, the test for ammonium ion must be tried before anything else is done. If it is allowed to stand, the unknown may pick up ammonia fumes from the air and give the test for ammonium ions.

84. The original solution should be tested with litmus before adding any reagents, and basic solutions should be reported as containing OH^- . A solid material may be treated with water and the aqueous solution used for this test.

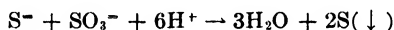
85. In neutral or alkaline solutions it is possible to have a mixture of S^{2-} , SO_3^{2-} , and $S_2O_3^{2-}$. These may be separated and identified in the following manner:

Add CdCO_3 to the solution, heat for 30 min. on the steam bath, then filter. Test the precipitate for sulfide.

To the filtrate from this treatment add an excess of SrCl_2 solution, rub the walls of the container with a stirring rod, then let stand at least 30 min. Filter. Test the precipitate for sulfites and the filtrate for thiosulfates in the usual manner.

86. In the presence of S^- or NO_2^- this test is not specific, as the H_2S and the NO_2 given off when sulfides and nitrites are acidified will bleach permanganates also. If the original solution is acid, however, there will be no conflict, for, as pointed out earlier, these ions cannot exist together in acid solutions.

87. If S^- were found present, the appearance of sulfur at this point does not necessarily mean $\text{S}_2\text{O}_3^{2-}$ are present. Sulfide ions react with sulfurous acid, in acid solution, as follows:



88. This reaction is specific for $\text{S}_2\text{O}_3^{2-}$ in the presence of SO_3^{2-} . It depends upon the fact that silver ions react with thiosulfates in neutral solutions to form $\text{Ag}_2\text{S}_2\text{O}_3$ which breaks down to form black Ag_2S .

89. A test recommended by C. Spacu and P. Spacu (34) is as follows:

To 1 drop of the prepared solution add 1 drop Ni^{++} test solution and 2 to 3 drops ethylenediamine. Stir, and let stand. If $\text{S}_2\text{O}_3^{2-}$ are present, a violet, crystalline precipitate will form. This test is specific as far as S^- , SO_3^{2-} , and SCN^- are concerned.

90. If SO_3^{2-} or $\text{S}_2\text{O}_3^{2-}$ are present, they must be destroyed by acidifying the solution with dilute H_3PO_4 , adding 1 to 2 drops 3*N* K_2CrO_4 solution and letting it stand for 2 to 3 min. This solution is then tested for CO_3^{2-} in the usual manner.

91. This test depends on the fact that the CO_2 given off reacts with the $\text{Ba}(\text{OH})_2$ to form insoluble BaCO_3 . Since the air in most laboratories contains a fairly large concentration of CO_2 , it is best to hold another drop of $\text{Ba}(\text{OH})_2$ solution near the apparatus and report CO_3^{2-} only if the drop above the reaction mixture becomes cloudy more quickly than does the blank test.

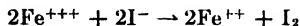
92. If interfering ions, such as SCN^- or $\text{Fe}(\text{CN})_6^{3-}$, are present, make the solution very slightly acid, suspend 1 drop 2*N* NaOH in the tip of a glass tube a short distance above the mixture and warm gently for 2 to 3 min.

Dip the end of the glass tube containing the NaOH , into 2 to 3 drops water and stir a moment. Using this solution, perform the test for cyanide as described.

93. The accurate analysis of solutions containing all six of the members of Group II is too involved to include here. For a more detailed outline of the procedure to use for such solutions, reference should be made to a more comprehensive text such as the treatise by Treadwell and Hall (22).

94. This test works only in the absence of I^- and $\text{Fe}(\text{CN})_6^{3-}$. The former

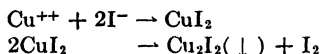
reduces Fe^{+++} to Fe^{++} , giving at the same time a yellow or brown solution of I_2 . The reaction is:



The $\text{Fe}(\text{CN})_6^{=}$ give a deep blue color or precipitate which covers up the red color of the $\text{Fe}(\text{SCN})_3$.

95. If the cation analysis showed copper to be present, it must be removed before applying this test. This may be done by the usual Group II metal sulfide precipitation. The filtrate from this should be boiled to expel H_2S and the test then applied.

96. If iodide ions were found present, treat 2 to 3 drops of the prepared solution with excess (about 5 drops) Cu^{++} test solution, warm, rub the inside of the container with a stirring rod, and let stand about 5 min. Filter, discarding the precipitate. Evaporate the filtrate barely to dryness, cool, and dissolve the residue in water. Use this solution in testing for Br^- . The reactions involved are:



An alternative method is to add 1 drop H_2O_2 and 5 drops CCl_4 to about 4 drops of the prepared solution, shake well, then withdraw the CCl_4 layer with a medicine dropper. Repeat this process until the CCl_4 layer is no longer colored violet or pink. If Br^- are present, the CCl_4 layer will then be yellow or orange.

97. This test does not work if SCN^- , $\text{Fe}(\text{CN})_6^{=}$, or $\text{Fe}(\text{CN})_6^{=}$ are present as these ions give a similar reaction. For the treatment of such cases, see a more comprehensive text.

98. If the cation analysis on this solution showed chromium is absent, chromates and dichromates need not be sought. However, if chromium is present, these test should be carried out.

If the original unknown gives an acid reaction with litmus, any positive results with these tests should be reported as $\text{Cr}_2\text{O}_7^{=}$; if alkaline, $\text{CrO}_4^{=}$ should be reported. Similarly, if S^- , $\text{CO}_3^{=}$, or $\text{SO}_3^{=}$ are found in a solution that was, originally, acid, they should be reported as HS^- , HCO_3^- , and HSO_3^- , respectively.

99. Unless the precipitate is definitely reddish or brownish in appearance, do not report $\text{CrO}_4^{=}$ on the basis of this test, as I^- , $\text{PO}_4^{=}$, and several other ions give yellow precipitates with Ag^+ .

100. The coin test shows merely that the precipitate contains sulfur. At this point in the procedure, however, it becomes specific for $\text{SO}_4^{=}$.

The use of this test prevents the analyst's being misled by a precipitate of BaF_2 in case F^- are present.

101. This test depends upon the fact that H_2S precipitates As_2S_3 very slowly from weakly acid solutions of arsenates, whereas it precipitates As_2S_3 readily, from solutions of arsenites (see pages 84 and 85).

102. As many organic compounds reduce alkaline copper solutions in a similar manner, this test is not always specific for arsenites. However,

with organic compounds eliminated, the test may be considered quite specific at this point in the procedure.

103. It is best to remove the excess of Ag^+ , from the AgNO_3 used in the preliminary treatment, before adding the NH_4OH . This is done by adding NH_4Cl solution and filtering, using the filtrate for the test described here.

104. In the tests described here, no distinction is made between $\text{BO}_3^{=}$ and B_4O_7^{-} . The reason for this is that acid solutions of B_4O_7^{-} contain some $\text{BO}_3^{=}$, and the tests used here are characteristic of these ions.

105. If the cation analysis showed copper to be present, it should be removed by the H_2S treatment described in Note 95. Copper compounds also give a green color to flames; and if it is not removed, this test may be misleading.

106. Iodide, thiocyanate, nitrite, chromate, ferrocyanide, and ferri-cyanide ions interfere with the "ring" test for nitrates. However, these have been removed by the preliminary treatment.

It is essential that care be taken to use the solution that was prepared especially for this test, as the other Group IV prepared solution always contains nitrate ions introduced when AgNO_3 was added to remove the Group II anions.

107. Another test for acetate ions is to evaporate 3 drops of the solution to dryness, add a little dry As_2O_3 and heat the mixture. A *very poisonous*, foul-smelling substance, cacodyl oxide, $((\text{CH}_3)_2\text{As})_2\text{O}$, is given off. This is a very sensitive test but is specific only in the absence of other organic acids.

108. When chlorates are treated with alkali and aluminum or zinc, the chlorate is reduced to chloride. Since any chloride ions present in the original unknown were removed during the preliminary treatments, the formation of AgCl at this point is a good test for ClO_3^{-} .

If excess AgNO_3 were added during the preliminary treatment, a white precipitate of AgCl may be found even before the AgNO_3 solution is added in this test. This, however, merely confirms the presence of ClO_3^{-} .

109. If the prepared solution, containing MnO_4^{-} , is made alkaline with NaOH before the H_2O_2 is added, the same evolution of oxygen will occur. In this case, however, a brown precipitate will form instead of the solution becoming colorless. This is due to the fact that MnO_4^{-} are reduced to $\text{MnO}_2 \cdot \text{H}_2\text{O}$ in alkaline solution instead of to Mn^{++} .

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APPENDIX

TABLE I.—OXIDATION-REDUCTION POTENTIALS*

| Electrode Reaction | E.m.f., Volts |
|---|---------------|
| $\text{Li} \rightarrow \text{Li}^+ + \epsilon$ | -2 959 |
| $\text{K} \rightarrow \text{K}^+ + \epsilon$ | -2 924 |
| $\text{Ca} \rightarrow \text{Ca}^{++} + 2\epsilon$ | -2 7 |
| $\text{Na} \rightarrow \text{Na}^+ + \epsilon$ | -2 714 |
| $\text{Mg} \rightarrow \text{Mg}^{++} + 2\epsilon$ | -2 40 |
| $\text{Al} \rightarrow \text{Al}^{+++} + 3\epsilon$ | -1 7 |
| $\text{Zn} + 2(\text{OH}^-) \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\epsilon$ | -1 248 |
| $\text{Mn} \rightarrow \text{Mn}^{++} + 2\epsilon$ | -1 1 |
| $\text{Tl} + \text{I}^- \rightarrow \text{TlI} + \epsilon$ | -0 77 |
| $\text{Zn} \rightarrow \text{Zn}^{++} + 2\epsilon$ | -0 76 |
| $\text{Pb} + 2(\text{OH}^-) \rightarrow \text{PbO} + \text{H}_2\text{O} + 2\epsilon$ | -0 57 |
| $\text{Cr} \rightarrow \text{Cr}^{++} + 2\epsilon$ | -0 55 |
| $\text{S}^- \rightarrow \text{S} + 2\epsilon$ | -0 51 |
| $\text{Fe} \rightarrow \text{Fe}^{++} + 2\epsilon$ | -0 44 |
| $\text{Cr}^{++} \rightarrow \text{Cr}^{+++} + \epsilon$ | -0 40 |
| $\text{Cd} \rightarrow \text{Cd}^{++} + 2\epsilon$ | -0 40 |
| $2\text{Cu} + 2(\text{OH}^-) \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\epsilon$ | -0 34 |
| $\text{Cu} + \text{H}_2\text{S} \rightarrow \text{CuS} + 2\text{H}^+ + 2\epsilon$ | -0 26 |
| $\text{Ni} \rightarrow \text{Ni}^{++} + 2\epsilon$ | -0 23 |
| $\text{Sb} + \text{H}_2\text{O} \rightarrow \text{SbO}^+ + 2\text{H}^+ + 3\epsilon$ | -0 21 |
| $\text{Cu}_2\text{O} + 2(\text{OH}^-) \rightarrow \text{CuO} + \text{H}_2\text{O} + 2\epsilon$ | -0 15 |
| $\text{Sn} \rightarrow \text{Sn}^{++} + 2\epsilon$ | -0 13 |
| $\text{Pb} \rightarrow \text{Pb}^{++} + 2\epsilon$ | -0 12 |
| $\text{Cu}_2\text{O} + 2(\text{OH}^-) + \text{H}_2\text{O} \rightarrow 2\text{Cu}(\text{OH})_2 + 2\epsilon$ | -0 08 |
| $2\text{Hg} + 2\text{I}^- \rightarrow \text{Hg}_2\text{I}_2 + 2\epsilon$ | -0 041 |
| $2\text{Ag} + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + 2\text{H}^+ + 2\epsilon$ | -0 036 |
| $\frac{1}{2}\text{H}_2 \rightarrow \text{H}^+ + \epsilon$ | ± 0 000 |
| $\text{Ag} + \text{Br}^- \rightarrow \text{AgBr} + \epsilon$ | + 0 073 |
| $\text{Hg} + 2(\text{OH}^-) \rightarrow \text{HgO} + \text{H}_2\text{O} + 2\epsilon$ | + 0 097 |
| $\text{Cu} + \text{Cl}^- \rightarrow \text{CuCl} + \epsilon$ | + 0 128 |
| $\text{Sn}^{++} \rightarrow \text{Sn}^{++++} + 2\epsilon$ | + 0 13 |
| $2\text{Sb} + 3\text{H}_2\text{O} \rightarrow \text{Sb}_2\text{O}_3 + 6\text{H}^+ + 6\epsilon$ | + 0 144 |
| $\text{H}_2\text{S} \rightarrow 2\text{H}^+ + \text{S} + 2\epsilon$ | + 0.17 |
| $\text{Bi} \rightarrow \text{Bi}^{+++} + 3\epsilon$ | + 0 2 |

* Most of these values were taken from the "International Critical Tables." In the cases where the values given in the above source were at wide variance with the values most widely accepted, these were changed to values reported in the literature, due consideration being given to the source of such information.

TABLE I.—OXIDATION-REDUCTION POTENTIAL.—(Continued)

| Electrode Reaction | E.m.f., Volts |
|--|---------------|
| $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \epsilon \dots$ | +0.222 |
| $\text{PbO} + 2(\text{OH}^-) \rightarrow \text{PbO}_2 + \text{H}_2\text{O} + 2\epsilon \dots$ | +0.27 |
| $\text{Cu} \rightarrow \text{Cu}^{++} + 2\epsilon \dots$ | +0.344 |
| $\text{Ti}^{++} \rightarrow \text{Ti}^{+++} + \epsilon \dots$ | +0.37 |
| $\text{CuCl}_2^- \rightarrow \text{Cu}^{++} + 2\text{Cl}^- + \epsilon \dots$ | +0.45 |
| $\text{Fe}(\text{CN})_6^{\equiv} \rightarrow \text{Fe}(\text{CN})_6^{\equiv} + \epsilon \dots$ | +0.486 |
| $2\text{Ag} + \text{CO}_3^- \rightarrow \text{Ag}_2\text{CO}_3 + 2\epsilon \dots$ | +0.50 |
| $\text{Cu} \rightarrow \text{Cu}^+ + \epsilon \dots$ | +0.51 |
| $\text{I}^- \rightarrow \frac{1}{2}\text{I}_2 + \epsilon \dots$ | +0.534 |
| $\text{AsO}_3^{\equiv} + \text{H}_2\text{O} \rightarrow \text{AsO}_4^{\equiv} + 2\text{H}^+ + 2\epsilon \dots$ | +0.574 |
| $2\text{Hg} + \text{SO}_4^- \rightarrow \text{Hg}_2\text{SO}_4 + 2\epsilon \dots$ | +0.621 |
| $\text{MnO}_4^- \rightarrow \text{MnO}_4^- + \epsilon \dots$ | +0.66 |
| $\text{Fe}^{++} \rightarrow \text{Fe}^{+++} + \epsilon \dots$ | +0.747 |
| $\text{Ag} \rightarrow \text{Ag}^+ + \epsilon \dots$ | +0.797 |
| $2\text{Hg} \rightarrow \text{Hg}_2^{++} + 2\epsilon \dots$ | +0.798 |
| $\text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2\epsilon \dots$ | +0.84 |
| $\text{Hg} \rightarrow \text{Hg}^{++} + 2\epsilon \dots$ | +0.86 |
| $\text{Br}^- \rightarrow \frac{1}{2}\text{Br}_2 + \epsilon \dots$ | +1.064 |
| $\frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O} \rightarrow \text{IO}_3^- + 6\text{H}^+ + 6\epsilon \dots$ | +1.19 |
| $\text{Tl}^+ \rightarrow \text{Tl}^{+++} + 2\epsilon \dots$ | +1.2 |
| $\text{Au} \rightarrow \text{Au}^{+++} + 3\epsilon \dots$ | +1.3 |
| $\text{Mn}^{++} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+ + 2\epsilon \dots$ | +1.33 |
| $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \epsilon \dots$ | +1.358 |
| $\text{Pb}^{++} + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + 4\text{H}^+ + 2\epsilon \dots$ | +1.44 |
| $\text{Au} \rightarrow \text{Au}^+ + \epsilon \dots$ | +1.5 |
| $2\text{SO}_4^- \rightarrow \text{S}_2\text{O}_8^{--} + 2\epsilon \dots$ | +1.5 |
| $\text{Mn}^{++} + 4\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 8\text{H}^+ + 5\epsilon \dots$ | +1.52 |
| $\text{MnO}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 4\text{H}^+ + 3\epsilon \dots$ | +1.58 |
| $\text{PbSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^- + 2\epsilon \dots$ | +1.679 |
| $\text{Co}^{++} \rightarrow \text{Co}^{+++} + \epsilon \dots$ | +1.8 |
| $\text{F}^- \rightarrow \frac{1}{2}\text{F}_2 + \epsilon \dots$ | +1.96 |

SOLUBILITY PRODUCT CONSTANTS*

| Salt | Temperature, °C. | Constant |
|----------------------------------|---------------------|-----------------------|
| AgBr | 25 | 7.7×10^{-13} |
| AgCl | 25 | 1.6×10^{-10} |
| AgCN | 20 | 2.7×10^{-12} |
| Ag ₂ CO ₃ | 25 | 8.2×10^{-12} |
| Ag ₂ CrO ₄ | 25 | 3.3×10^{-12} |
| AgI | 25 | 1.5×10^{-16} |
| BaCO ₃ | 25 | 8×10^{-9} |
| BaCrO ₄ | 25 | 2.2×10^{-10} |
| BaSO ₄ | 25 | 1.0×10^{-10} |
| CaCO ₃ | 25 | 8×10^{-8} |
| CaC ₂ O ₄ | 25 | 2.6×10^{-9} |
| CaF ₂ | 25 | 3.8×10^{-11} |
| CaSO ₄ | 25 | 2.3×10^{-4} |
| MgCO ₃ | 12 | 1.9×10^{-4} |
| Mg(OH) ₂ | 18 | 2×10^{-11} |
| PbCO ₃ | 18 | 3.3×10^{-14} |
| PbCrO ₄ | 18 | 1.8×10^{-14} |
| PbSO ₄ | 18 | 1.0×10^{-8} |
| SrCO ₃ | 25 | 1.6×10^{-9} |
| SrCrO ₄ | 25 | 3.6×10^{-5} |
| SrSO ₄ | 25 | 2.8×10^{-7} |
| Ag ₂ S | . | 10^{-50} |
| CuS | . | 10^{-42} |
| FeS | . | 10^{-19} |
| HgS | . | 10^{-54} |
| MnS | . | 10^{-15} |
| PbS | . | 10^{-28} |
| ZnS | . | 1.2×10^{-23} |

* Hammett, "Solutions of Electrolytes" (1929).

IONIZATION CONSTANTS*

| Reaction | Temperature, °C. | Constant |
|---|---------------------|-----------------------|
| $\text{H}_3\text{BO}_3 = \text{H}^+ + \text{H}_2\text{BO}_3^-$ | 25 | 6.5×10^{-10} |
| $\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$ | 25 | 3.3×10^{-7} |
| $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$ | 25 | 3.9×10^{-11} |
| $\text{HCN} = \text{H}^+ + \text{CN}^-$ | 25 | 7.2×10^{-10} |
| $\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$ | 18 | 8.3×10^{-3} |
| $\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$ | 18 | 2×10^{-7} |
| $\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$ | 18 | 4×10^{-13} |
| $\text{HNO}_2 = \text{H}^+ + \text{NO}_2^-$ | 18 | 4.5×10^{-4} |
| $\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$ | 25 | 1.15×10^{-2} |
| $\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$ | 18 | 9×10^{-8} |
| $\text{HS}^- = \text{H}^+ + \text{S}^{2-}$ | 18 | 1×10^{-15} |
| $\text{H}_2\text{SO}_3 = \text{H}^+ + \text{HSO}_3^-$ | 25 | 1.2×10^{-2} |
| $\text{HSO}_3^- = \text{H}^+ + \text{SO}_3^{2-}$ | 25 | 5×10^{-6} |
| $\text{HC}_2\text{H}_3\text{O}_2 = \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$ | 25 | 1.86×10^{-5} |
| $\text{NH}_4\text{OH} = \text{NH}_4^+ + \text{OH}^-$ | 25 | 1.8×10^{-5} |

* Hammett, "Solutions of Electrolytes" (1929)

LIST OF APPARATUS*

Number (per student):

- 2 Beakers, one 250 ml. and one 400 ml.
- 1 Beaker rack. Made by boring six holes $\frac{1}{2}$ in. diameter and $\frac{1}{2}$ in. deep about 2 in. apart (center to center) in a softwood block 8 by 4 by 1 in.
- 1 Bottle (about $4\frac{1}{2}$ in. high and capable of taking a No. 6 or 7 rubber stopper).
- Centrifuge, hand or electrical (1 for each 10 to 12 students).
- 1 Clamp (screw).
- Cotton, absorbent.
- 2 Crucibles, 10 ml.
- 1 Cylinder, graduated, 10 ml.
- 2 Dishes, evaporating, 60 mm.
- Filter paper (2 doz. sheets, acid-treated).
- 1 File, triangular.
- 1 Flask, Florence 500 ml. (to be made into wash bottle with capillary tip).
- 6 Glass rods, 1 to 2 mm. by 15 cm. long.
- 1 Lead dish (about 2 cm. diameter and 1 cm. deep. May be shaped from a 1 in. square of $\frac{1}{16}$ in. sheet lead).
- 12 Medicine droppers.
- 12 Microscope slide.
- 1 Rubber stopper, No. 7.
- 1 Rubber stopper, No. 2.
- 1 Spot plate
- 1 Steam bath (may be made by boring three holes capable of taking

* It is desirable to have individual reagent kits whenever possible, as this saves much time in the laboratory. These kits may be either purchased or made. A convenient kit is made by arranging two blocks about 8 by 12 by 1 in. thick, with holes bored in each to accommodate 50 vials each. About 80 of the vials should be arranged with dropper tops (see Reagent Containers) for dispensing liquids; about 20 of the vials should have ordinary cork or screw tops for holding solids.

About 10 of the vials should have a capacity of 30 ml. each. These hold the reagents most commonly used, such as HCl, HNO₃, H₂C₂H₃O₂, H₂SO₄, saturated NH₄C₂H₃O₂, saturated NH₄Cl, etc. The other vials should have a capacity of 8 ml. each.

If individual reagents kits are not available, the reagents may be placed in 4-oz. dropper-type bottles on the side shelf for use by the whole class.

- a No. 7 cork in the lid of a $\frac{1}{2}$ -pint "Karo" sirup can, fitting them with corks bored to loosely hold the microbeakers. A hole should be bored in the side of the can near the top to act as a steam outlet).
- 20 Test tubes, soft glass 4 by $\frac{1}{2}$ in. (or 18 Pyrex test tubes 75 by 10 mm., and two 4 by $\frac{1}{2}$ -in. Pyrex test tubes).
- 1 Test tube, soft glass, 6 by $\frac{3}{4}$ in.
- 1 Test tube, Pyrex, 6 by $\frac{3}{4}$ in.
- 1 Tongs, or forceps.
- 2 ft. Tubing, glass, 6 mm O.D.
- 2 ft. Tubing, glass, 10 to 12 mm.
- 1 ft. Tubing, rubber.
- 1 Wire gauze.
- 1 Wire triangle.

In addition to the apparatus listed above, blowpipes, platinum wires, standard small ring stands fitted with rings and small burette clamps, and Bunsen burners should be available. The latter may be used as micro-burners by unscrewing the burner tube and lighting the gas at the orifice in the base. In this way the Bunsen burner serves two purposes.

Experience has shown that the small electrically driven centrifuges with angle type head, which have been designed for semi-micro work, are more convenient and economical of time and cost than the less expensive hand-operated ones.

LIST OF REAGENTS

(All chemicals should be reagent grade)

REAGENTS FOR CATIONS

SOLID REAGENTS

Acid, gallic
Aluminum (granular, As free)
Ammonium chloride
Ammonium iodide
Ammonium persulfate
Ammonium sulfate
Borax (c.p.)
Ferrous sulfide (sticks) (see Hydrogen Sulfide Generator)
Potassium chlorate (c.p. crystals)
Sodium carbonate (anhydrous, c.p.)
Sodium cobaltinitrite
Sodium hydroxide (c.p. pebble form)
Sodium thiosulfate
Sulfur-paraffin mixture (see Hydrogen Sulfide Generator)
Thiosinamine (allyl thiourea)

LIQUID REAGENTS AND SOLUTIONS

Acid, acetic
 Concentrated (approximately 17*N*)
 Dilute (6*N*)
 Dilute (exactly 1*N*)
Acid, hydrochloric
 Concentrated (approximately 13*N*)
 Dilute (6*N*)
Acid, nitric
 Concentrated (approximately 16*N*)
 Dilute (6*N*)
Acid, picric
 Saturated aqueous solution
Acid, sulfuric
 Concentrated (approximately 36*N*)
 Dilute (6*N*)
 Dilute (1:4. Made by adding 1 volume of concentrated acid to
 4 volumes of water)

Acid, tartaric

10 g. acid to 100 ml. water

Alcohol, ethyl (95 per cent)

Alizarin S (blue)

Dissolve 0.05 g. in 100 ml. of 50 per cent acetone and add 2 drops glacial acetic acid

Aluminon, $C_{19}H_9O_2(COONH_4)_3$

Dissolve 0.1 g. of aluminon (the ammonium salt of aurin tricarboxylic acid) in 100 ml. water

Ammonium acetate

Saturated solution in water

A 2.5*N* solution (18 g. dissolved in a little water and the solution diluted to 100 ml. A better way of preparing this is to mix equal volumes of exactly 5*N* acetic acid and 5*N* ammonium hydroxide)

Ammonium benzoate (7 per cent)

Dissolve 7 g. in 100 ml. water

Ammonium carbonate reagent

Dissolve 20 g. ammonium carbonate and 30 g. NH_4Cl in 100 ml. 6*N* NH_4OH

Ammonium carbonate

Dissolve 15 g. ammonium carbonate in a mixture of 8 ml. concentrated ammonium hydroxide and 50 ml. water, then dilute to 100 ml.

Ammonium chloride

Saturated solution in water

1*N* solution (5.35 g. dissolved in water and diluted to 100 ml.)

Ammonium hydroxide

Concentrated (approximately 15*N*)

Dilute (6*N*)

Ammonium nitrate

Wash solution. Dissolve 8 g. in 100 ml. water

Ammonium sulfate

Wash solution. Dissolve 13 g. in 100 ml. water

Ammonium thiocyanate

Dissolve 8 g. in 100 ml. water

Barium chloride

Dissolve 2 g. of the anhydrous salt (or 2.4 g. of the dihydrate) in 100 ml. water

Benzidine

Dissolve 0.05 g. of the pure substance in 10 ml. glacial acetic acid and add 90 ml. water

α -Benzoinoxime

Dissolve 5 g. in 100 ml. ethyl alcohol.

Bromine water

Saturated solution in water

Cacotheline

Saturated solution in water

Cinchonine

Dissolve 1 g. of reagent in 100 ml. water, add about 10 drops nitric acid, and warm until dissolved. Cool, and add 2 g. of solid KI

Copper sulfate (0.1 per cent)

Dissolve 0.1 g. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 100 ml. water

Dimethylglyoxime

Dissolve 1 g. in 100 ml. ethyl alcohol

Diphenylcarbazide

Prepare 100 ml. of a saturated solution of reagent in 50 per cent acetone. Filter and saturate with KSCN. Then add 1 g. KI

Ether, diethyl**Hydrogen peroxide (3 per cent)****Mercuric chloride**

Dissolve 2.7 g. in 100 ml. water

Mercuric chloride-ammonium thiocyanate reagent $(\text{NH}_4)_2\text{Hg}(\text{SCN})_4$

Dissolve 30 g. of ammonium thiocyanate in 100 ml. water, then add 27 g. of HgCl_2 , and stir until dissolved

p-Nitrobenzeneazoresorcinol

Dissolve 0.001 g. in 100 ml. 0.5 per cent NaOH and filter if necessary

 α -Nitroso- β -naphthol

Dissolve 1 g. in 50 ml. glacial acetic acid and add 50 ml. water

Potassium chromate (3N)

Dissolve 58.2 g. of K_2CrO_4 in enough water to make 100 ml. solution

Potassium cyanide (3 per cent)

Dissolve 3 g. in enough water to make 100 ml.

Potassium ferrocyanide

Dissolve 8.5 g. in 100 ml. water

Potassium iodide

0.1N solution. Dissolve 1.7 g. in 100 ml. water

Saturated solution in water

Potassium oxalate (3N)

Dissolve 55 g. in 100 ml. water

Potassium sulfate (0.3N)

Dissolve 5.2 g. in 100 ml. water

Potassium thiocyanate

Dissolve 10 g. in 100 ml. water

Pyridine (pure)**Rhodanine (dimethylaminobenzal rhodanine)**

Dissolve 0.03 g. in 100 ml. acetone

Silver nitrate

1 per cent solution. Dissolve 1 g. AgNO_3 in 100 ml. water

50 per cent solution. Dissolve 50 g. of AgNO_3 in 100 ml. water

Stannous chloride

Dissolve 10 g. in 100 ml. concentrated hydrochloric acid and add two or three pieces of tin to each bottle

Sodium acetate

Saturated solution in water

Sodium bicarbonate

Dissolve 8.4 g. in 100 ml. water

Sodium bisulfite (0.1*N*)

Dissolve 1 g. in 100 ml. water

Sodium hydroxide (6*N*)

Dissolve 24 g. of NaOH in 100 ml. water

Sodium phosphate (Na_2HPO_4)

Dissolve 10 g. of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in 100 ml. water

Zinc uranyl acetate

Dissolve 10 g. of uranyl acetate and 30 g. of zinc acetate in 100 ml. 3 per cent acetic acid. Let stand over night and filter

ADDITIONAL REAGENTS FOR ANION ANALYSIS**Alcohol, amyl****Alcohol, methyl****Ammonium molybdate reagent**

Dissolve 4 g. MoO_3 in 20 ml. 6*N* NH_4OH , add 75 ml. 6*N* HNO_3 , and dilute to a volume of 100 ml.

Ammonium polysulfide

Saturate 100 ml. 6*N* NH_4OH with H_2S , add 1 g. sulfur, and shake vigorously.

Barium chloride-calcium chloride reagent

Dissolve 24 g. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and 22 g. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 ml. of water

Barium hydroxide

Saturated solution

Carbon tetrachloride**Copper nitrate (0.1*N*)**

Dissolve 1.2 g. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 75 ml. water, add 10 drops concentrated HNO_3 and dilute to 100 ml.

Diphenylamine reagent

Dissolve 0.4 g. diphenylamine in 100 ml. 80 per cent H_2SO_4

Ferric chloride (0.05*N*)

Dissolve 0.5g. of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 70 ml. water, add 5 ml. concentrated HCl , and dilute to 100 ml.

Ferrous ammonium sulfate

Dissolve 2 g. $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in 80 ml. water, add 3 ml. 6*N* H_2SO_4 , and dilute to 100 ml.

Iodine solution

Saturated solution.

Lanthanum nitrate

Dissolve 4 g. $\text{La}(\text{NO}_3)_3$ in 100 ml. water

Lead acetate (0.1*N*)

Dissolve 1.9 g. $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ in 80 ml. water, add 1 ml. glacial acetic acid, and dilute to 100 ml.

Magnesia mixture

Dissolve 10 g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 g. NH_4Cl in 40 ml. water, add 50 ml. concentrated NH_4OH , and dilute to 100 ml.

Potassium permanganate

Dissolve 0.5 g. KMnO_4 in 100 ml. water and add 3 ml. concentrated H_2SO_4

Silver carbonate (solid)

Starch-potassium iodide paper

Turmeric solution

Saturated solution in 95 per cent alcohol

TEST SOLUTIONS AND UNKNOWNNS

In making up unknowns and test solutions, some instructors want the solution to contain a definite *weight* of the cation or the anion in a given volume. Others, wishing to emphasize the laws of chemistry rather than the practical aspects of analysis, prefer that the solutions have a standard *molarity*, as most of the calculations in theory are made using the concentrations of solutions in mols per liter.

Semi-micro methods do not require any special concentrations for their use. The usual concentrations can be used in semi-microanalysis as well as they could in macroanalysis.

For the instructors convenience, however, the following table is included, giving the weights of the salts of different cations needed to make a solution of the cation for test solutions and unknowns.

It is suggested that these cation stock solutions be diluted 1:9 in actual use.

Anion test solutions should be $0.1M$, as a rule. Anion unknowns should be made from stock solutions that are $0.5M$ with the sodium or potassium salts of the desired anions.

On an average it will be found that 50 ml. of each test solution and 50 ml. of each stock solution for making unknowns will be more than ample for 40 students, during a one-semester course.

| Metal | Formula of salt | Weight of salt per 100 ml. to make | |
|--|--|------------------------------------|-------------------------------|
| | | 0.1M, grams | 100 mg. per milliliter, grams |
| Aluminum | $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | 3 75 | 69 |
| Antimony* | SbCl_3 | 2 28 | 18 7 |
| Arsenic† | As_2O_3 | 0.98 | 13 |
| Barium | $\text{Ba}(\text{NO}_3)_2$ | 2 61 | 19 |
| Bismuth‡ | $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ | 4 85 | 23 3 |
| Cadmium | $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ | 3 08 | 27 5 |
| Calcium | $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ | 2 36 | 59 |
| Chromium | $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | 4 00 | 77 |
| Cobalt | $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 2 91 | 49 5 |
| Copper§ | $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ | 2 41 | 38 3 |
| Iron§ | $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | 4 04 | 72.3 |
| | $\text{FeSO}_4 (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ | 3 92 | 70.2 |
| Lead§ | $\text{Pb}(\text{NO}_3)_2$ | 3 31 | 16 |
| Magnesium | $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 2 56 | 106 |
| Manganese | $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 2.87 | 52 3 |
| Mercury (Hg^{++})§ | $\text{Hg}(\text{NO}_3)_2$ | 3 24 | 15 7 |
| Mercury (Hg_2^{++}) | $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ | 2 80 | 13 6 |
| Nickel | $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 2 90 | 49 6 |
| Potassium | KNO_3 | 1 01 | 25 6 |
| Silver | AgNO_3 | 1 69 | 15.8 |
| Sodium | NaNO_3 | 0 85 | 37 |
| Strontium | $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ | 2 83 | 32 5 |
| Tin (Sn^{++++})† | $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ | 3 14 | 26 4 |
| Tin (Sn^{++})¶ | $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ | 2 25 | 19 |
| Zinc§ | $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | 2 97 | 45 4 |

* Use 6N HCl as the solvent.

† Dissolve in hot 6N HCl.

‡ Dissolve in 3N HNO_3 .

§ Dissolve in water, then add 1 ml concentrated HNO_3 to each 100 ml of solution.

|| Dissolve in 100 ml. water and add 3 ml. concentrated HNO_3 and a small globule of metallic mercury.

¶ Dissolve in 50 ml. concentrated HCl, dilute to 100 ml, and add a little pure metallic tin.

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